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PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

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NEWS
      1
                 Web Page for STN Seminar Schedule - N. America
NEWS
         OCT 02
                 CA/CAplus enhanced with pre-1907 records from Chemisches
                 Zentralblatt
NEWS
         OCT 19
      3
                 BEILSTEIN updated with new compounds
         NOV 15
NEWS
                 Derwent Indian patent publication number format enhanced
NEWS
      5
         NOV 19
                 WPIX enhanced with XML display format
NEWS
      6
         NOV 30
                 ICSD reloaded with enhancements
         DEC 04
NEWS
      7
                 LINPADOCDB now available on STN
NEWS
      8
         DEC 14
                 BEILSTEIN pricing structure to change
NEWS
     9
         DEC 17
                 USPATOLD added to additional database clusters
NEWS 10
         DEC 17
                 IMSDRUGCONF removed from database clusters and STN
NEWS 11
         DEC 17
                 DGENE now includes more than 10 million sequences
NEWS 12
         DEC 17
                 TOXCENTER enhanced with 2008 MeSH vocabulary in
                 MEDLINE segment
NEWS 13
         DEC 17
                 MEDLINE and LMEDLINE updated with 2008 MeSH vocabulary
NEWS 14
                 CA/CAplus enhanced with new custom IPC display formats
         DEC 17
NEWS 15
         DEC 17
                 STN Viewer enhanced with full-text patent content
                 from USPATOLD
NEWS 16
         JAN 02
                 STN pricing information for 2008 now available
NEWS 17
         JAN 16
                 CAS patent coverage enhanced to include exemplified
                 prophetic substances
NEWS 18
         JAN 28
                 USPATFULL, USPAT2, and USPATOLD enhanced with new
                 custom IPC display formats
NEWS 19
         JAN 28
                 MARPAT searching enhanced
NEWS 20
         JAN 28
                 USGENE now provides USPTO sequence data within 3 days
                 of publication
NEWS 21
         JAN 28
                 TOXCENTER enhanced with reloaded MEDLINE segment
                 MEDLINE and LMEDLINE reloaded with enhancements
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         JAN 28
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                 STN Express, Version 8.3, now available
         FEB 08
NEWS 24
         FEB 20
                 PCI now available as a replacement to DPCI
NEWS 25
         FEB 25
                 IFIREF reloaded with enhancements
NEWS 26
         FEB 25
                 IMSPRODUCT reloaded with enhancements
NEWS 27
                 WPINDEX/WPIDS/WPIX enhanced with ECLA and current
         FEB 29
                 U.S. National Patent Classification
NEWS 28
         MAR 31
                 IFICDB, IFIPAT, and IFIUDB enhanced with new custom
                 IPC display formats
                 CAS REGISTRY enhanced with additional experimental
NEWS 29
         MAR 31
                 spectra
NEWS 30
         MAR 31
                 CA/CAplus and CASREACT patent number format for U.S.
                 applications updated
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         MAR 31
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NEWS EXPRESS FEBRUARY 08 CURRENT WINDOWS VERSION IS V8.3,
             AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008
NEWS HOURS
              STN Operating Hours Plus Help Desk Availability
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              Welcome Banner and News Items
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\* \* \* \* \* \* \* \* \* \* \* STN Columbus

FILE 'HOME' ENTERED AT 18:09:38 ON 01 APR 2008

=> FILE REG

COST IN U.S. DOLLARS

TOTAL SINCE FILE ENTRY SESSION 0.21 0.21

FULL ESTIMATED COST

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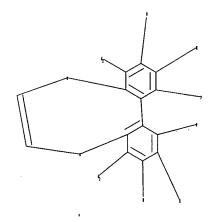
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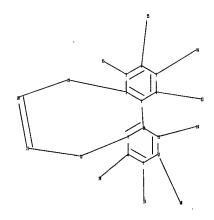
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chain nodes :
13  14  15  16  17  18  23  24
ring nodes :
1  2  3  4  5  6  7  8  9  10  11  12  19  20  21  22
chain bonds :
3-13  4-15  5-16  6-23  7-17  8-14  11-24  12-18
ring bonds :
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19-20  20-21  21-22
exact/norm bonds :
1-10  2-19  3-13  8-14  9-22  19-20  20-21  21-22
exact bonds :
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normalized bonds :
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```

G1:C1,Br,F,I

G2:H,C1,Br,F,I

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom 12:Atom 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:CLASS 19:Atom 20:Atom 21:Atom 22:Atom 23:CLASS 24:CLASS

≒> S L1 FULL

FULL SEARCH INITIATED 18:10:17 FILE 'REGISTRY' FULL SCREEN SEARCH COMPLETED -2139 TO ITERATE

100.0% PROCESSED 2139 ITERATIONS

SEARCH TIME: 00.00.01

L2 1 SEA SSS FUL L1

=> FILE CAPLUS

COST IN U.S. DOLLARS

SINCE FILE TOTAL ENTRY SESSION 178.57

178.36

1 ANSWERS

FULL ESTIMATED COST

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=> S L2

L3 1 L2

=> D L3 IBIB ABS HITSTR 1

ANSWER 1 OF 1 CAPLUS COPYRIGHT 2008 ACS on STN

2001:228894 CAPLUS ACCESSION NUMBER:

DOCUMENT NUMBER: 134:266437

TITLE: Chiral phosphines, transition metal complexes thereof

and uses thereof in asymmetric reactions

INVENTOR(S): Zhang, Xumu

PATENT ASSIGNEE(S): Penn State Research Foundation, USA

SOURCE: PCT Int. Appl., 52 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.					KIND		DATE			APPLICATION NO.					DATE		
TIO 2001 021 625				7.1		00010200											
MO 5001051652				AI		20010329			WO 2000-US25635					20000919			
	W:	ΑE,	ΑG,	AL,	AM,	ΑT,	ΑU,	ΑZ,	BA,	BB,	BG,	BR,	BY,	ΒZ,	CA,	CH,	CN,
		CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EE,	ES,	FI,	GB,	GD,	GE,	GH,	GM,	HR,
		ΗU,	ID,	IL,	IN,	IS,	JP,	ΚE,	KG,	ΚP,	KR,	ΚZ,	LC,	LK,	LR,	LS,	LT,
		LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NO,	NZ,	PL,	PT,	RO,	RU,

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             YU, ZA, ZW
         RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY,
             DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ,
             CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG
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PRIORITY APPLN. INFO.:
                                             US 1999-154845P
                                                                     19990920
                                             WO 2000-US25635
                                                                  W 20000919
OTHER SOURCE(S):
                         CASREACT 134:266437; MARPAT 134:266437
GI
```

Ι

AB Chiral ligands and transition metal complexes based on such chiral ligands useful in asym. catalysis are disclosed. The chiral ligands include chiral C1-C6-TunaPhos ligands I (n = 1-6). The ruthenium TunaPhos complex reduces ketones to the corresponding alcs. with 95-99.6 % enantioselectivity. The transition metal complexes of the chiral ligands are useful in asym. reactions such as asym. hydrogenation, hydride transfer, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, hydrocarboxylation, isomerization, allylic alkylation, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition and epoxidn. reactions.

IT 331768-60-6

RL: CAT (Catalyst use); USES (Uses) (preparation of chiral diphosphines as cocatalyst in transition metal complex catalyzed asym. reactions)

RN 331768-60-6 CAPLUS
CN Phosphine, (14aR)-tribenzo[b,e,g][1,4]dioxocin-1,14-diylbis[diphenyl-(9CI) (CA INDEX NAME)

=>

---Logging off of STN---

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Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
•	ENTRY	SESSION
FULL ESTIMATED COST	5.93	184.50
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
·	ENTRY	SESSION
CA SUBSCRIBER PRICE	-0.80	-0.80

STN INTERNATIONAL LOGOFF AT 18:11:08 ON 01 APR 2008



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      1
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                 Zentralblatt
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      3
         OCT 19
                 BEILSTEIN updated with new compounds
NEWS
      4
         NOV 15
                 Derwent Indian patent publication number format enhanced
NEWS
      5
         NOV 19
                 WPIX enhanced with XML display format
         NOV 30
NEWS
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      7
NEWS
         DEC 04
                 LINPADOCDB now available on STN
NEWS
      8
         DEC 14
                 BEILSTEIN pricing structure to change
     9
NEWS
         DEC 17
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NEWS 10
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NEWS 13
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                 MEDLINE and LMEDLINE updated with 2008 MeSH vocabulary
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                 STN Viewer enhanced with full-text patent content
                 from USPATOLD
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                 STN pricing information for 2008 now available
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                 prophetic substances
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         JAN 28
                 USPATFULL, USPAT2, and USPATOLD enhanced with new
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         JAN 28
                 MARPAT searching enhanced
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NEWS 25
         FEB 25
                 IFIREF reloaded with enhancements
NEWS 26
         FEB 25
                 IMSPRODUCT reloaded with enhancements
                 WPINDEX/WPIDS/WPIX enhanced with ECLA and current
NEWS 27
         FEB 29
                 U.S. National Patent Classification
         MAR 31
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                 IFICDB, IFIPAT, and IFIUDB enhanced with new custom
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NEWS 30
         MAR 31
                 CA/CAplus and CASREACT patent number format for U.S.
                 applications updated
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         MAR 31
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             AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008
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NEWS LOGIN
              Welcome Banner and News Items
NEWS IPC8
              For general information regarding STN implementation of IPC 8
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COST IN U.S. DOLLARS
SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST
0.21
0.21

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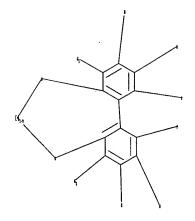
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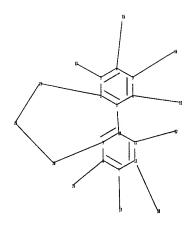
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chain nodes :
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ring nodes :
1  2  3  4  5  6  7  8  9  10  11  12  19  20  26
chain bonds :
3-13  4-15  5-16  6-21  7-17  8-14  11-22  12-18
ring bonds :
1-2  1-6  1-10  2-3  2-19  3-4  4-5  5-6  7-8  7-12  8-9  9-10  9-20  10-11  11-12
19-26  20-26
exact/norm bonds :
1-2  1-6  1-10  2-3  2-19  3-13  8-14  9-10  9-20  10-11  19-26  20-26
exact bonds :
4-15  5-16  6-21  7-17  11-22  12-18
normalized bonds :
3-4  4-5  5-6  7-8  7-12  8-9  11-12
```

G1:Cl,Br,F,I

G2:H,C1,Br,F,I

Match level:
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom
11:Atom 12:Atom 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:CLASS 19:Atom 20:Atom 21:CLASS 22:CLASS 26:CLASS

#### L1STRUCTURE UPLOADED

=> S L1 FULL

FULL SEARCH INITIATED 18:19:54 FILE 'REGISTRY' FULL SCREEN SEARCH COMPLETED -9 TO ITERATE

100.0% PROCESSED

9 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

L2

.]

O SEA SSS FUL L1

=> FILE CAPLUS

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

SESSION

FULL ESTIMATED COST

ENTRY 178.36 178.57

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=> S L2

L3

0 L2

=>

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=> LOG Y

COST IN U.S. DOLLARS

SINCE FILE ENTRY TOTAL

FULL ESTIMATED COST

0.48

SESSION 179.05

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PASSWORD:

TERMINAL (ENTER 1, 2, 3, OR ?):2

```
Welcome to STN International
NEWS
                 Web Page for STN Seminar Schedule - N. America
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NEWS
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                 CA/CAplus enhanced with pre-1907 records from Chemisches
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                 CA/CAplus enhanced with new custom IPC display formats
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         DEC 17
                 STN Viewer enhanced with full-text patent content
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                 of publication
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NEWS 32
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                 EMBASE, EMBAL, and LEMBASE reloaded with enhancements
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             AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008
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              STN Operating Hours Plus Help Desk Availability
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NEWS LOGIN
NEWS IPC8
              For general information regarding STN implementation of IPC 8
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=> FILE REG

COST IN U.S. DOLLARS

FULL ESTIMATED COST

SINCE FILE TOTAL ENTRY SESSION 0.84 0.84

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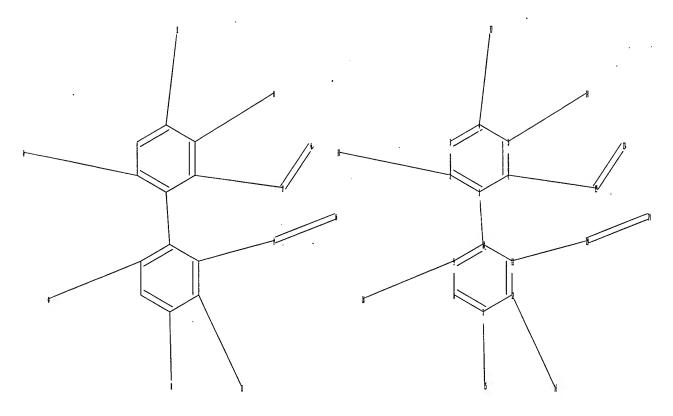
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chain nodes:
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ring nodes:
1 2 3 4 5 6 7 8 9 10 11 12
chain bonds:
1-10 2-17 4-13 5-14 6-19 7-15 9-18 11-20 12-16 19-23 20-24
ring bonds:
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exact/norm bonds:
2-17 9-18 19-23 20-24
exact bonds:
1-10 4-13 5-14 6-19 7-15 11-20 12-16
normalized bonds:
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12

G1:C1, Br, F, I

G2:H,C1,Br,F,I

## Match level:

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom 12:Atom 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:Atom 18:Atom 19:CLASS 20:CLASS 23:CLASS 24:CLASS

### L1 STRUCTURE UPLOADED

=> D L1

L1 HAS NO ANSWERS

L1 STR

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

Structure attributes must be viewed using STN Express guery preparation.

=> S L1 FULL

FULL SEARCH INITIATED 08:42:03 FILE 'REGISTRY' FULL SCREEN SEARCH COMPLETED - 737 TO ITERATE

100.0% PROCESSED 737 ITERATIONS 127 ANSWERS

SEARCH TIME: 00.00.01

L2127 SEA SSS FUL L1

=> FILE CAPLUS

COST IN U.S. DOLLARS TOTAL SINCE FILE ENTRY SESSION FULL ESTIMATED COST 178.82 179.66

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=> S L2

31 L2 L3

=> D L3 IBIB ABS HITSTR 1-31

ANSWER 1 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2007:1053337 CAPLUS

DOCUMENT NUMBER:

147:365607

TITLE:

SOURCE:

Process for recovery of phosphorus-containing ligands from metal compounds with phosphine ligands used as

homogeneous catalysts by sequential oxidation,

extraction and isolation steps

INVENTOR(S):

Schlummer, Bjoern; Scholz, Ulrich; Risch, Nikolaus.;

Majoros, Laszlo

PATENT ASSIGNEE(S):

Saltigo GmbH, Germany; Universitaet Paderborn

Eur. Pat. Appl., 14pp.

CODEN: EPXXDW

DOCUMENT TYPE:

Patent German

LANGUAGE: FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO. KIND DATE APPLICATION NO. \_\_\_\_ ----- EP 1834695 A1 20070919 EP 2007-4910 20070309
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE,
IS, IT, LI, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR,
AL, BA, HR, MK, YU

DE 102006011867 A1 20070920 DE 2006-102006011867 20060315 US 20080021245 A1 20080124 US 2007-716914 20070312 PRIORITY APPLN. INFO.: DE 2006-102006011867A 20060315

OTHER SOURCE(S): CASREACT 147:365607; MARPAT 147:365607

Phosphine ligands R1PR2R3 [R1, R2, R3 = (un)substituted C1-8 alkyl, aryl, aralkyl; substituents, e.g., C1, Br, iodo, F; C1-8 alkyl, aryl or aralkyl; NO2, alkoxy, aryloxy] are recovered from reaction mixts. upon completion of the reaction in which transition metal complexes with phosphine ligands, preferably Ru, Pd, Re or Pt complexes, are used as homogeneous catalysts by sequentially contacting the residual reaction mixture with an oxidizing agent, preferably H2O2, NaClO, O2, halogen oxide derivs., S8 or Se, extraction of the reaction mixture with an organic solvent immiscible with

mixture, preferably a halogenated hydrocarbon such as CH2Cl2, an ether such as Bu2O, an alc., or an aromatic compound such as PhMe, to sep. out the transition-metal oxide thus produced, and isolation of the oxidized phosphine from the organic solvent separated from the reaction mixture, e.g.,

recrystn.; the oxidized phosphine thus obtained can be treated with a reductant such as H2 or a halosilane to give the original phosphine.

E.g., after 0.08 mmol (1%) [RuBr2(L)] [L = 5,5'-dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl] was used as the homogeneous catalyst in hydrogenation of Et acetoacetate, the residue from distillation of product was treated with 1 mL 35% aqueous H2O2, stirred 1 h, then treated with 25 mL more water and extracted with 3 mL Bu2O and heated 2 h at 140°; subsequent removal of Ru oxide by filtration and removal of solvent afforded 56% of the bis-oxide of L.

IT 185836-54-8P

RL: SPN (Synthetic preparation); PREP (Preparation) (process for recovery of P-containing ligands from metal compds. with phosphine ligands used as homogeneous catalysts by sequential oxidation, extraction and isolation steps)

RN 185836-54-8 CAPLUS

CN Phosphine oxide, [3',5-dichloro-6'-(diphenylphosphinyl)-2',6-dimethoxy[1,1'-biphenyl]-2-yl]diphenyl- (CA INDEX NAME)

REFERENCE COUNT: 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 2 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:72653 CAPLUS

DOCUMENT NUMBER: 146:337264

TITLE: Iron Porphyrin-Catalyzed Olefination of Ketenes with Diazoacetate for the Enantioselective Synthesis of

Allenes

AUTHOR(S): Li, Chuan-Ying; Wang, Xiao-Bing; Sun, Xiu-Li; Tang, Yong; Zheng, Jun-Cheng; Xu, Zheng-Hu; Zhou, Yong-Gui;

Dai, Li-Xin

CORPORATE SOURCE: State Key Laboratory of Organometallic Chemistry,

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, Peop. Rep.

China

SOURCE: Journal of the American Chemical Society (2007),

129(6), 1494-1495

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:337264

AB In the presence of Ph3P and catalytic Fe(TCP)Cl, ketenes R1R2C:C:O (R1 = Br, EtO2C, n-Bu, Ph, 4-ClC6H4, etc.; R2 = H, Me, Et, Me2CH, allyl, etc.) could react with Et diazoacetate to give allenes R1R2C:C:CHCO2Et in high yields under neutral conditions. By employing a chiral phosphine instead of PPh3, allenes could be synthesized with high enantioselectivity (93-98% ee) in good yields.

IT 929007-26-1P

RL: PUR (Purification or recovery); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (asym. synthesis of ethoxycarbonyl-substituted allenes via iron porphyrin-catalyzed olefination of ketenes with diazoacetate)

RN 929007-26-1 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(3-methoxyphenyl)- (CA INDEX NAME)

IT 928835-63-6P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(asym. synthesis of ethoxycarbonyl-substituted allenes via iron porphyrin-catalyzed olefination of ketenes with diazoacetate)

RN 928835-63-6 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-bis(3-methoxyphenyl)- (CA INDEX NAME)

REFERENCE COUNT: 65 THERE ARE 65 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 3 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:1119878 CAPLUS

DOCUMENT NUMBER: 147:211951

TITLE: Synthesis of new MeO-BIPHEP-type chiral diphosphines

by an improved way

AUTHOR(S): Ma, Meng-Lin; Peng, Zong-Hai; Chen, Li; Guo, Yu; Chen,

Hua; Li, Xian-Jun

CORPORATE SOURCE: Key Laboratory of Green Chemistry and Technology of

Ministry of Education, Institute of Homogeneous Catalysis, Faculty of Chemistry, Sichuan University,

Chengdu, Sichuan, 610064, Peop. Rep. China

SOURCE: Chinese Journal of Chemistry (2006), 24(10), 1391-1396

CODEN: CJOCEV; ISSN: 1001-604X

PUBLISHER: Shanghai Institute of Organic Chemistry

Ι

DOCUMENT TYPE: Journal LANGUAGE: Fnglish

LANGUAGE: English

AB New optically active MeO-BIPHEP-type ligands, (S)-6.6'-dimethoxy-2,2'-bis(di-p-alkoxyphenyl-phosphine)-1,1'-biphenyl (S)-I [n = 0, 3, 7, 11, 15 (S)-5b-(S)-5e] were prepared and characterized. Starting from the com. available tri-Et phosphite and m-bromoanisole, an optically active (S)-6.6'-dimethoxybiphenyl-2,2'-diyl-bis(phosphonic acid diester) was prepared by an improved way and converted to the corresponding dichlorides, which was used as a key intermediate to react with p-alkoxybenzenemagnesium bromide or p-alkoxyphenyl Li to directly give the

RN 145265-44-7 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

RN 945028-74-0 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(4-butoxyphenyl)- (CA INDEX NAME)

RN 945028-76-2 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis[4-(octyloxy)phenyl]- (CA INDEX NAME)

RN 945028-78-4 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis[4-(dodecyloxy)phenyl]- (CA INDEX NAME)

RN 945028-80-8 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis[4-(hexadecyloxy)phenyl]- (CA INDEX NAME)

IT 145209-14-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(resolution; preparation and conversion of chiral

dimethoxybiphenyldiylbis(phos

phonic acid diester) using aryl Grignard or lithium reagents to give enantiomerically pure biphenyl diphosphine ligands)

RN 145209-14-9 CAPLUS

CN Phosphonic acid, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, P,P,P',P'-tetraethyl ester (CA INDEX NAME)

REFERENCE COUNT:

27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 4 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2006:433679 CAPLUS

DOCUMENT NUMBER:

145:82847

TITLE:

Use of 1H NMR chemical shifts to determine the absolute configuration and enantiomeric purity for

enantiomers of 3,3'-disubstituted-MeO-BIPHEP

derivatives

AUTHOR(S):

Gorobets, Evgueni; Parvez, Masood; Wheatley, Bronwen

M. M.; Keay, Brian A.

CORPORATE SOURCE:

Department of Chemistry, University of Calgary,

Calgary, AB, T2N 1N4, Can.

SOURCE:

Canadian Journal of Chemistry (2006), 84(2), 93-98

CODEN: CJCHAG; ISSN: 0008-4042

PUBLISHER:

National Research Council of Canada

DOCUMENT TYPE: LANGUAGE:

Journal English

The absolute configuration of a series of 3,3'-disubstituted-MeO-BIPHEP derivs. (I; R= H, MeO,i-PrO,o-t-Bu,OPiv, Otolyl, i-Pr,Ph,mesityl) can be determined by the 1H NMR chemical shift of the methoxyl group when the 3,3'-disubstituted-MeO-BIPHEP derivative is mixed with (-)-(2R,3R)-dibenzoyltartaric acid ((-)-DBTA) (1:2) and its NMR spectrum is run in CDCl3. The chemical shift of the methoxyl group in the Sax enantiomer always occurred at higher field than the corresponding Rax enantiomer. Integration of the corresponding methoxyl signals provides the enantiomeric purity of any mixts.

IT 133577-82-9 133577-84-1

RL: PRP (Properties)

Ι

(use of  $\overline{\mathsf{IH}}$  NMR chemical shifts to determine absolute configuration and enantiomeric

purity for enantiomers of 3,3'-disubstituted-MeO-BIPHEP derivs.)

RN 133577-82-9 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-84-1 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

IT 894100-06-2P 894100-13-1P

RL: PRP (Properties); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation)

(use of 1H NMR chemical shifts to determine absolute configuration and enantiomeric  $% \left( 1\right) =\left( 1\right) +\left( 1\right)$ 

purity for enantiomers of 3,3'-disubstituted-MeO-BIPHEP derivs.)

RN 894100-06-2 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, (2R,3R)-, compd. with (1R)-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (2:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-82-9 CMF C38 H32 O4 P2

CM 2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 894100-13-1 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, (2R,3R)-, compd. with [(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenylphosphine oxide] (2:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-84-1 CMF C38 H32 O4 P2

CM 2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

IT 133545-15-0

RL: RCT (Reactant); RACT (Reactant or reagent)
(use of 1H NMR chemical shifts to determine absolute configuration and enantiomeric

purity for enantiomers of 3,3'-disubstituted-MeO-BIPHEP derivs.)

RN 133545-15-0 CAPLUS

Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1diphenyl- (CA INDEX NAME)

REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

ANSWER 5 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2006:328224 CAPLUS

DOCUMENT NUMBER:

145:62371

TITLE:

CN

A new class of versatile chiral-bridged atropisomeric

diphosphine ligands: remarkably efficient ligand

syntheses and their applications in highly enantioselective hydrogenation reactions

AUTHOR(S):

Qiu, Liqin; Kwong, Fuk Yee; Wu, Jing; Lam, Wai Har;

Chan, Shusun; Yu, Wing-Yiu; Li, Yue-Ming; Guo, Rongwei; Zhou, Zhongyuan; Chan, Albert S. C.

CORPORATE SOURCE:

Open Laboratory of Chirotechnology of the Institute of

Molecular Technology for Drug Discovery and Synthesis and Department of Applied Biology and Chemical

Technology, Hong Kong Polytechnic University, Hong

Kong, Hong Kong

SOURCE:

Journal of the American Chemical Society (2006),

128(17), 5955-5965

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER:

American Chemical Society

DOCUMENT TYPE:

Journal English

LANGUAGE: GΙ

# \* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

A series of chiral diphosphine ligands denoted as PQ-Phos (I, II, and III; n = 0, 1, 2) was prepared by atropdiastereoselective Ullmann coupling and ring-closure reactions. The Ullmann coupling reaction of the biaryl diphosphine dioxides (IV; n = same as above) is featured by highly efficient central-to-axial chirality transfer with diastereomeric excess >99%. This substrate-directed diastereomeric biaryl coupling reaction is unprecedented for the preparation of chiral diphosphine dioxides, and our method precludes the tedious resolution procedures usually required for preparing enantiomerically pure diphosphine ligands. The effect of chiral recognition was also revealed in a relevant asym. ring-closure reaction of (S) - or (R)-HO-BIPHEPO (V) or (VI) with chiral alkanediol dimesylate or ditosylate (VII; R = Ms, n = 0; R = Ts, n = 1 or 2). The chiral tether bridging the two aryl units creates a conformationally rigid scaffold essential for enantiofacial differentiation; fine-tuning of the ligand scaffold (e.g., dihedral angles) can be achieved by varying the chain length of the chiral tether. The enantiomerically pure Ru- and Ir-PQ-Phos complexes have been prepared and applied to the catalytic enantioselective hydrogenations of  $\alpha$ - and  $\beta$ -ketoesters (C:O bond reduction) of formula R1COCO2R2 (R1 = Me or Ph, R2 = Me; R1 = Me, iso-Pr, Ph, or PhCH2CH2) and R1COCHR2CO2R3 (R1 = Me, R2 = H, R3 = Me, Et, or CH2Ph; R1 = C1CH2 or Ph, R2 = H, R3 = Et; R1 = Ph, R2 = C1, R3 = Et) to chiral  $\alpha$ - or  $\beta$ -hydroxy esters of formula R1CH(OH)CO2R2 and R1CH(OH)CHR2CO2R3, 2-(6'-methoxy-2'-naphthyl)propenoic acid, alkyl-substituted  $\beta$ -dehydroamino acids (C:C bond reduction) of formula R2O2CCH:C(R1)NHAc (R1 = Me, Et, iso-Pr, or tert-Bu, R2 = me; R1 = Me or n-Pr, R2 = Et) to chiral  $\beta$ -amino acid esters of formula R2O2CCH2CHC(R1)NHAc, and N-heteroarom. compds. (C:N bond reduction) (VIII; R1 = Me, R2 = Me, H, MeO; R1 = Ph, R2 = H), (IX), and (X) to chiral heterocyclic compds. (XI), (XII), and (XIII). An excellent level of enantioselection (up to 99.9% ee) has been attained for the catalytic reactions. In addition, the significant ligand dihedral angle effects on the Ir-catalyzed asym. hydrogenation of N-heteroarom. compds. were also revealed.

133577-84-1DP, ruthenium complexes
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
USES (Uses)

(preparation of versatile chiral-bridged atropisomeric diphosphine ligands by stereoselective ring-closure of (S)- or (R)-HO-BIPHEPO with chiral alkanediol dimesylate or ditosylate)

RN 133577-84-1 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-84-1 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

IT 524711-75-9P 679422-50-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of versatile chiral-bridged atropisomeric diphosphine ligands by stereoselective ring-closure of (S)- or (R)-HO-BIPHEPO with chiral alkanediol dimesylate or ditosylate)

RN 524711-75-9 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1R)- (9CI) (CA INDEX NAME)

RN 679422-50-5 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1S)- (9CI) (CF INDEX NAME)

REFERENCE COUNT:

130 THERE ARE 130 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

ANSWER 6 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN L3

ACCESSION NUMBER:

2006:219844 CAPLUS

DOCUMENT NUMBER:

146:62793

TITLE:

Improvement on the synthesis of chiral biphenyl

diphosphine ligands

AUTHOR (S):

Fang, Chun-Mei; Ma, Meng-Lin; Zheng, Xue-Li; Guo, Yu;

Peng, Zong-Hai; Chen, Hua; Li, Xian-Jun

CORPORATE SOURCE:

Key Laboratory of Green Chemistry and Technology of

Ministry of Education, Institute of Homogeneous Catalysis, Department of Chemistry, Sichuan University, Chengdu, 610064, Peop. Rep. China

SOURCE:

Youji Huaxue (2006), 26(2), 252-255

CODEN: YCHHDX; ISSN: 0253-2786

PUBLISHER:

Youji Huaxue Bianjibu

DOCUMENT TYPE:

Journal

LANGUAGE:

Chinese

OTHER SOURCE(S):

CASREACT 146:62793

The chiral diphosphines, R- and S-(6,6'-dimethoxy)-2,2'bis(diarylphosphino)-1,1'-biphenyl, (aryl = Ph, 4-C6H4OMe) have been prepared with six steps from com. available 3-bromoanisole by a concise synthetic route. This approach was also an efficient synthetic method for biphenyl diphosphines with different diarylphosphino groups.

IT 133577-82-9P 133577-84-1P 145265-43-6P

145265-44-7P

RL: PUR (Purification or recovery); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of chiral biphenyl diphosphine ligands starting from bromoanisole)

133577-82-9 CAPLUS RN

Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-CN diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-84-1 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 145265-43-6 CAPLUS .

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

RN 145265-44-7 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

IT 133545-15-0P 145209-14-9P 145209-18-3P

145209-27-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of chiral biphenyl diphosphine ligands starting from bromoanisole)

RN 133545-15-0 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-diphenyl- (CA INDEX NAME)

RN 145209-14-9 CAPLUS

CN Phosphonic acid, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, P,P,P',P'-tetraethyl ester (CA INDEX NAME)

RN 145209-18-3 CAPLUS

CN Phosphonic dichloride, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-(CA INDEX NAME)

RN 145209-27-4 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

PAGE 1-A

PAGE 2-A

L3 ANSWER 7 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:208444 CAPLUS

DOCUMENT NUMBER: 144:450471

TITLE: Diastereospecific Intramolecular Ullmann Couplings:

Unique Chiral Auxiliary for the Preparation of

3,3'-Disubstituted MeO-BIPHEP Derivatives
Gorobets, E: McDonald R: Keay R A

AUTHOR(S): Gorobets, E.; McDonald, R.; Keay, B. A.

CORPORATE SOURCE: Department of Chemistry, University of Calgary,

Calgary, T2N 1N4, Can.

SOURCE: Organic Letters (2006), 8(7), 1483-1485

CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:450471

AB A chiral auxiliary is described that provides only one diastereomer during intramol. Ullmann couplings. Treatment of five Ullmann coupling precursors with Cu powder in DMF at 115 °C provides

2,2',3,3',6,6'-hexasubstituted 1,1'-biphenyls as single diastereomers in yields ranging from 66% to 91%.

IT 133577-84-1P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of 3,3'-disubstituted MeO-BIPHEP derivs. by diastereospecific intramol. Ullmann couplings using a unique chiral auxiliary)

RN 133577-84-1 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-bipheny1]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

REFERENCE COUNT:

THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 8 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:88172 CAPLUS

DOCUMENT NUMBER: 145:396761

TITLE: Dendritic BIPHEP: Synthesis and application in

asymmetric hydrogenation of  $\beta\text{-keto}$  esters

AUTHOR(S): Deng, Guo-Jun; Li, Guo-Rui; Zhu, Ling-Yun; Zhou,

Hai-Feng; He, Yan-Mei; Fan, Qing-Hua; Shuai, Zhi-Gang

CORPORATE SOURCE: Laboratory of Chemical Biology, Center for Molecular

Science, Institute of Chemistry, Chinese Academy of

Sciences, Beijing, 100080, Peop. Rep. China

SOURCE: Journal of Molecular Catalysis A: Chemical (2006),

244(1-2), 118-123

CODEN: JMCCF2; ISSN: 1381-1169

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE:

Journal

LANGUAGE:

English

OTHER SOURCE(S):

CASREACT 145:396761

A series of new chiral dendritic biphenyldiphosphine ligands were prepared and their applications in the Ru-catalyzed asym. hydrogenation of  $\beta$ -keto esters were investigated. Ruthenium catalysts containing these dendrimer ligands were effective in the hydrogenation of  $\beta$ -keto

esters. The size of the dendritic wedges influenced the

enantioselectivity significantly.

IT 524711-75-9P 911438-18-1P 911438-19-2P

911438-20-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of dendritic biphenyldiphosphine ligands for ruthenium-catalyzed asym. hydrogenation of  $\beta$ -keto esters)

RN 524711-75-9 CAPLUS

[1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1R)- (9CI) (CA) CN INDEX NAME)

RN 911438-18-1 CAPLUS

Phosphine oxide, [(1R)-6,6'-bis[[3,5-bis(phenylmethoxy)phenyl]methoxy][1,1 CN '-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 911438-19-2 CAPLUS

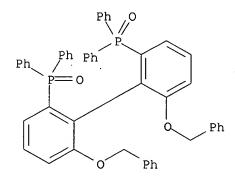
CN Phosphine oxide, [(1R)-6,6'-bis[[3,5-bis[[3,5-bis[[3,5-bis(phenylmethoxy)phenyl]methoxy]]]] Phosphine oxide, [(1R)-6,6'-bis[[3,5-bis[[3,5-bis([5,5-bis([5

PAGE 1-A

PAGE 2-B

RN 911438-20-5 CAPLUS

Phosphine oxide, [(1R)-6,6'-bis(phenylmethoxy)[1,1'-biphenyl]-2,2'diyl]bis[diphenyl- (9CI) (CA INDEX NAME)



REFERENCE COUNT:

70 THERE ARE 70 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

ANSWER 9 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2005:621820 CAPLUS

DOCUMENT NUMBER:

143:286065

TITLE:

CN

Cu(I)-Catalyzed Direct Enantioselective Cross

AUTHOR(S):

Aldol-Type Reaction of Acetonitrile Suto, Yutaka; Tsuji, Riichiro; Kanai, Motomu;

Shibasaki, Masakatsu

CORPORATE SOURCE:

Graduate School of Pharmaceutical Sciences, The

University of Tokyo, Tokyo, 113-0033, Japan

SOURCE:

Organic Letters (2005), 7(17), 3757-3760

CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER:

American Chemical Society

DOCUMENT TYPE:

Journal

LANGUAGE:

English

OTHER SOURCE(S):

CASREACT 143:286065

Direct catalytic enantioselective cross aldol-type reaction of aldehydes RCHO (R = Me2CHCH2, cyclohexyl, Ph, PhCH2, n-hexyl, etc.) with acetonitrile to give  $\beta$ -hydroxynitriles RCHOHCH2CN was developed using Cu alkoxide-chiral phosphine complexes as catalysts. Chemoselective activation and deprotonation of the donor substrate (acetonitrile) by the soft metal alkoxide in a strongly donating solvent (HMPA) are key to success in this reaction. Useful chemical yields and promising enantioselectivities are produced using either DTBM-SEGPHOS or a tuned BIPHEP as a chiral ligand.

IT 864365-86-6P

RL: PUR (Purification or recovery); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(Preparation of hiphenyl dipherphine as chiral ligand for Cu(I)-cat

(preparation of biphenyl diphosphine as chiral ligand for Cu(I)-catalyzed direct cross aldol-type reaction of aldehydes with acetonitrile)

RN 864365-86-6 CAPLUS

Butanedioic acid, 2,3-bis(benzoyloxy)-, (2S,3S)-, compd. with tetraethyl [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[phosphonate] (1:1) (9CI) (CA INDEX NAME)

CM 1

CN

CRN 145264-54-6 CMF C22 H32 O8 P2

CM 2

CRN 17026-42-5 CMF C18 H14 O8

Absolute stereochemistry. Rotation (+).

RN 145265-39-0 CAPLUS
CN Phosphonic dichloride, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(9CI) (CA INDEX NAME)

RN 864365-87-7 CAPLUS
CN Phosphine oxide, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[bis[4-(1-methylethoxy)-3,5-bis(1-methylethyl)phenyl]- (9CI) (CA INDEX NAME)

REFERENCE COUNT:

SOURCE:

32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

CAPLUS COPYRIGHT 2008 ACS on STN L3 ANSWER 10 OF 31

2005:378835 CAPLUS ACCESSION NUMBER:

DOCUMENT NUMBER: 143:78246

TITLE: Avoiding the classical resolution during the synthesis

of MeO-BIPHEP and 3,3'-disubstituted derivatives

Gorobets, Evgueni; Wheatley, Bronwen M. M.; Hopkins, AUTHOR(S):

J. Matthew; McDonald, Robert; Keay, Brian A.

CORPORATE SOURCE: Department of Chemistry, University of Calgary,

Calgary, AB, T2N 1N4, Can. Tetrahedron Letters (2005), 46(22), 3843-3846

CODEN: TELEAY; ISSN: 0040-4039

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English OTHER SOURCE(S): CASREACT 143:78246

The Ullmann coupling of a (S)-2-acetoxy propionyl chloride-derived iododiphenylphosphinyl benzene derivative gave a a 2:1 mixture of diastereomers in 81% yield that are easily separated by silica gel chromatog. This procedure avoids the generally cumbersome and sometimes difficult resolution step with DBTA. Similar Ullmann couplings and separation of the corresponding diastereomers are employed with other (S)-2-acetoxy propionyl chloride-derived iodo diphenylphosphinyl benzene derivs. or (R)-2-acetoxy propionyl chloride-derived iodo diphenylphosphinyl benzene derivs. ultimately affording a new series of 3,3'-disubstituted-MeO-BIPHEP derivs. The use of these new derivs. in a palladium-catalyzed asym. Heck reaction, a Pd-catalyzed asym. polyene cyclization reaction, and a rhodium-catalyzed

enantioselective hydrogenation is also reported.

IT . 855300-66-2P

RL: SPN (Synthetic preparation); PREP (Preparation)
(minor diastereomer formed in the preparation of a nonracemic biphenyldiphosphine using the stereoselective Ullmann coupling of a (diphenylphosphinyl)iodophenyl ester of (S)-acetyllactic acid as the key step)

RN 855300-66-2 CAPLUS

CN Propanoic acid, 2-(acetyloxy)-, (1S)-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl ester, (2S,2'S)- (9CI) (CA INDEX NAME)

IT 133577-82-9P 855300-65-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of nonracemic biphenyldiphosphines using the stereoselective Ullmann coupling of (diphenylphosphinyl)iodophenyl esters of acetyllactic acids as the key step)

RN 133577-82-9 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 855300-65-1 CAPLUS

CN Propanoic acid, 2-(acetyloxy)-, (1R)-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl ester, (2S,2'S)- (9CI) (CA INDEX NAME)

REFERENCE COUNT:

21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

CAPLUS COPYRIGHT 2008 ACS on STN ANSWER 11 OF 31

ACCESSION NUMBER:

2005:253273 CAPLUS

DOCUMENT NUMBER:

142:316957

TITLE:

Preparation of chiral biphenyl-2,2'-diyl diphosphines

substituted by alkoxycarbonyl groups for use in asymmetric hydrogenation of ketones and imines

INVENTOR(S):

Artl, Dieter; Meseguer, Benjamin

PATENT ASSIGNEE(S):

Bayer Chemicals A.-G., Germany Eur. Pat. Appl., 20 pp.

SOURCE:

CODEN: EPXXDW

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND DATE	APPLICATION NO.	DATE				
EP 1516880	A1 20050323	EP 2004-21174	20040907				
R: AT, BE, CH,	DE, DK, ES, FR,	GB, GR, IT, LI, LU,	NL, SE, MC, PT,				
IE, SI, LT,	LV, FI, RO, MK,	CY, AL, TR, BG, CZ,	EE, HU, PL, SK, HR				
DE 10342672	A1 20050421	DE 2003-10342672	20030916				
JP 2005089462	A 20050407	JP 2004-267421	. 20040914				
US 20050085377	A1 20050421	US 2004-940785	20040914				
PRIORITY APPLN. INFO.:		DE 2003-10342672	A 20030916				
OTHER SOURCE(S):	MARPAT 142:3169	57 ·					
GI							

Chiral (1R)- and (1S)-1,1'-biphenyl-2,2'-bis(phosphines) (I, Z = none, X = noneAB H, Cl, Br; R1 = R2 = Ph, cyclohexyl, 3,5-tBu-4-MeOC6H2, 3,5-Me2-4-MeOC6H2, 3,5-tBu2C6H3, 4-FC6H4; R3 = R4 = RO2CCH2, RO2CCHMe, where R = Me, Et; or

R3 = cyclohexyl, R4 = RO2CCH2, RO2CCHMe, same R), useful as ligands for asym. hydrogenation of prochiral ketones and imines (no data) and acetoacetate, were prepared by demethylation of corresponding phosphine oxides I (Z = O; R3 = R4 = Me, same X, R1, R2), followed by etherification of 6,6'-diols with R3Y, preferably cyclohexyl bromide, and RO2CCH2Br or RO2CCHMeBr and reduction by HSiCl3 and used as ligands for asym. hydrogenation of Et acetoacetate and Et chloroacetate. In an example, compound (S)-I (Z = O, X = Cl, R3 = R4 = H, R1 = R2 = Ph) was prepared by reaction of the corresponding dimethoxy-derivative with BBr3, followed by water hydrolysis; the diol was reacted with MeO2CH2Br to give I (Z = O, X = Cl, R3 = R4 = MeO2CCH2, R1 = R2 = Ph), which was reduced by HSiCl3 to give the corresponding diphosphine I (5, Z = none, same X, R1-R4). Asym. hydrogenation of Me acetoacetate in the presence of 0.02 mol% of 5 and 0.01 mol% of RuCl3 in ethanol under 90 atm of H2 for 1 h at 80° gave Me 3-hydroxybutyrate with 97.4 % ee.

IT 185913-95-5

RL: RCT (Reactant); RACT (Reactant or reagent)
(demethylation; preparation of axial-chiral biphenyl-2,2'-diphosphines
containing alkoxycarbonylalkoxy groups as ligands for asym. hydrogenation
of ketones)

RN 185913-95-5 CAPLUS

CN Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

IT 679422-50-5P 691363-03-8P 848078-14-8P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(etherification; preparation of axial-chiral biphenyl-2,2'-diphosphines containing alkoxycarbonylalkoxy groups as ligands for asym. hydrogenation of ketones)

RN 679422-50-5 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1S)- (9CI) (CA INDEX NAME)

RN 691363-03-8 CAPLUS
CN [1,1'-Biphenyl]-2,2'-diol, 3,3'-dichloro-6,6'-bis(diphenylphosphinyl)-,
(1S)- (9CI) (CA INDEX NAME)

RN 848078-14-8 CAPLUS
CN [1,1'-Biphenyl]-2-ol, 2'-(cyclohexyloxy)-6,6'-bis(diphenylphosphinyl)-,
(1S)- (9CI) (CA INDEX NAME)

ketones)

RN 848078-16-0 CAPLUS

CN Propanoic acid, 2,2'-[[(1S)-3,3'-dichloro-6,6'bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-, dimethyl ester (9CI) (CA INDEX NAME)

RN 848078-17-1 CAPLUS

CN ' Propanoic acid, 2,2'-[[(1S)-3,3'-dichloro-6,6'bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-, dimethyl ester, (2R,2'S)- (9CI) (CA INDEX NAME)

848078-12-6P 848078-13-7P 848078-15-9P ΙT

> RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(reduction; preparation of axial-chiral biphenyl-2,2'-diphosphines containing

> alkoxycarbonylalkoxy groups as ligands for asym. hydrogenation of ketones)

RN

848078-12-6 CAPLUS Acetic acid, 2,2'-[[(1S)-3,3'-dichloro-6,6'-bis(diphenylphosphinyl)[1,1'-CN biphenyl]-2,2'-diyl]bis(oxy)]bis-, dimethyl ester (9CI) (CA INDEX NAME)

RN

848078-13-7 CAPLUS
Acetic acid, 2,2'-[[(1S)-3,3'-dichloro-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-, diethyl ester (9CI) (CA INDEX NAME) CN

RN

848078-15-9 CAPLUS Acetic acid, [[(1S)-2'-(cyclohexyloxy)-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2-yl]oxy]-, methyl ester (9CI) (CA INDEX NAME) CN

REFERENCE COUNT:

5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT ANSWER 12 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:159895 CAPLUS

DOCUMENT NUMBER: 142:240572

TITLE: Preparation of allyloxybiphenyl phosphorus ligands for

enantioselective catalysis

INVENTOR(S):

Arlt, Dieter

PATENT ASSIGNEE(S):

Germany

SOURCE:

Ger. Offen., 5 pp.

CODEN: GWXXBX

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE		
DE 10335950 PRIORITY APPLN. INFO.:	A1	20050224	DE 2003-10335950 DE 2003-10335950	20030804		
				20030604		
OTHER SOURCE(S):	CASRE	ACT 142:2405	72; MARPAT 142:240572			

$$R^3R^4C = CR^5R^6R^7C$$
HO
 $P(O)_nR^1R^2$ 

Ι

Preparation of 6,6'-bis-allyloxybiphenyl derivs., I (R1, R2 = alkoxy, aryloxy, AB alkyl, cycloalkyl, aryl, hetaryl, etc.; R3-R7 = H, alkyl, aryl, etc.; Y = H, alkyl, alkoxy, etc.; n = 0-1), contained phosphorus in 2 and 2'-position, useful as ligands for transition metal complexes, which are useful as catalysts for enantioselective hydrogenations and isomerizations, is described. These rearrangement products, if they are present in chiral form, can be converted by a new isomerization procedure into mixts. of the atropisomers. Thus, reaction of (R)-(6,6'dihydroxybiphenyl-2,2'-diyl) bis(diphenylphosphine oxide) with K2CO3 in DMF gave 90.7% (R)-(6,6'-bisallyloxybiphenyl-2,2'-diyl) bis (diphenylphosphine oxide).

TΤ 524711-75-9

> RL: RCT (Reactant); RACT (Reactant or reagent) (preparation of allyloxybiphenyl phosphorus ligands for transition metal catalyzed enantioselective catalysis)

524711-75-9 CAPLUS RN

[1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1R)- (9CI) CN INDEX NAME)

IT 844679-25-0P 844679-26-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of allyloxybiphenyl phosphorus ligands for transition metal catalyzed enantioselective catalysis)

RN 844679-25-0 CAPLUS

CN Phosphine oxide, [(1R)-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 844679-26-1 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-3,3'-di-2-propenyl-, (1R)- (9CI) (CA INDEX NAME)

IT 844450-47-1P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of allyloxybiphenyl phosphorus ligands for transition metal catalyzed enantioselective catalysis)

RN 844450-47-1 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-3,3'-di-2-propenyl-(9CI) (CA INDEX NAME)

$$Ph-P-Ph$$
  $Ph-P-Ph$ 
 $H_2C$ — $CH-CH_2$   $CH_2-CH$ — $CH_2$ 

L3. ANSWER 13 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2005:58129 CAPLUS

DOCUMENT NUMBER:

142:137081

TITLE:

Preparation of biphenyldiphosphine compounds useful in

asymmetric reactions

INVENTOR(S):

Chan, Albert Sun-chi; Qiu, Liqin

PATENT ASSIGNEE(S):

The Hong Kong Polytechnic University, Hong Kong

SOURCE:

U.S. Pat. Appl. Publ., 18 pp. CODEN: USXXCO

DOCUMENT TYPE:

Patent

LANGUAGE:

English

Ι

FAMILY ACC. NUM. COUNT: 1

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE		
US 20050014633	A1	20050120	US 2004-888820	20040709		
US 7094725	B2	20060822				
PRIORITY APPLN. INFO.:			US 2003-486496P P	20030711		
OTHER SOURCE(S):	MARPAT	142:137081				
GI						

AB The present invention provides compds. of the formula I wherein R = optionally substituted lower alkyl, cycloalkyl or aryl; R' = alkyl or aryl; n = 0, 1, or 2; or an enantiomer thereof; or an enantiomeric mixture thereof. The compds. of formula I are bridged C2-sym. biphenyldiphosphine analogs and, thus, may be employed as ligands to generate chiral transition metal catalysts which may be applied in a variety of asym. reactions. The compds. of the present invention are easily accessible in

high diastereomeric and optical purity according to the methods disclosed herein.

IT 524711-75-9P 679422-50-5P

RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)

(preparation of biphenyldiphosphine compds. useful in asym. reactions)

RN 524711-75-9 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1R)- (9CI) (CA INDEX NAME)

RN 679422-50-5 CAPLUS
CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1S)- (9CI) (CA

IT 133577-82-9 133577-84-1

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of biphenyldiphosphine compds. useful in asym. reactions)

RN 133577-82-9 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN133577-84-1 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'diyl]bis[1,1-diphenyl- (CA INDEX NAME)

ANSWER 14 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN 2004:1127391 CAPLUS

ACCESSION NUMBER:

DOCUMENT NUMBER:

TITLE:

142:56522

INVENTOR(S):

Chiral ligands for application in asymmetric syntheses

Meseguer, Benjamin; Arlt, Dieter

PATENT ASSIGNEE(S):

Bayer Chemicals Ag, Germany

SOURCE:

PCT Int. Appl., 28 pp.

CODEN: PIXXD2

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.					KIND DATE		į	APPLICATION NO.					DATE				
WO 2004111063 WO 2004111063				A2 20041223 A3 20050331			1	WO 2004-EP5930					20040602				
		CN, GE, LK, NO, TJ, BW,	CO, GH, LR, NZ, TM, GH,	CR, GM, LS, OM, TN, GM,	CU, HR, LT, PG, TR, KE,	CZ, HU, LU, PH, TT, LS,	AU, DE, ID, LV, PL, TZ, MW,	DK, IL, MA, PT, UA, MZ,	DM, IN, MD, RO, UG, NA,	DZ, IS, MG, RU, US, SD,	EC, JP, MK, SC, UZ, SL,	EE, KE, MN, SD, VC, SZ,	EG, KG, MW, SE, VN, TZ,	ES, KP, MX, SG, YU, UG,	FI, KR, MZ, SK, ZA, ZM,	GB, KZ, NA, SL, ZM, ZW,	GD, LC, NI, SY, ZW AM,
	1032° 1033°	EE, SI, SN, 7109	ES,	FI, TR, TG	FR,	GB, BJ,	RU, GR, CF, 2004:	HU, CG,	IE, CI,	IT,	LU, GA, 003-1	MC, GN, 1032	NL, GQ, 7109	PL, GW,	PT, ML,	RO,	SE, NE,

```
EP 1636243
                                 20060322
                                             EP 2004-739512
                          A2
                                                                     20040602
             AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
             IE, SI, FI,
                         RO, CY, TR, BG, CZ, EE, HU, PL, SK
     JP 2006527221
                                                                     20040602
                           Т
                                 20061130
                                             JP 2006-515817
     US 20060161022
                           A1
                                 20060720
                                             US 2005-298641
                                                                     20051208
     US 20070004927
                           Α1
                                 20070104
                                             US 2006-571722
                                                                     20060313
PRIORITY APPLN. INFO.:
                                             DE 2003-10327109
                                                                     20030613
                                                                  Α
                                             DE 2003-10337013
                                                                  Α
                                                                     20030812
                                             WO 2004-EP5930
                                                                     20040602
OTHER SOURCE(S):
                          CASREACT 142:56522; MARPAT 142:56522
GI
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Ι

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The invention relates to the preparation of biarylbisphosphines I (B =
AB
     (CHR1)n(R2C:CR3)(CHR4)m, R1-R4 = H, alkyl, n, m = 1-8; G = Cl, H; R', R''
     = aryl, alkyl) and intermediates thereof. Furthermore, the invention
     relates to catalysts produced from the biarylbisphosphines and the use
     thereof in asym. syntheses. Thus, reaction of (S)-[5,5'-dichloro-6,6'-
     dihydroxybiphenyl-2,2'-diyl]bis(diphenylphosphine oxide) with allyl
     chloride in DMF in the presence of K2CO3 gave (S)-[5,5'-dichloro-6,6'-(1,4-
     but-2-enedioxy)biphenyl-2,2'-diyl]bis(diphenylphosphine oxide) as
     cocatalyst for ruthenium catalyzed enantioselective hydrogenation.
     810674-60-3P 810674-92-1P 810674-93-2P
IT
     810674-94-3P 810674-95-4P 810674-96-5P
     810674-97-6P 810674-98-7P 810674-99-8P
     810675-00-4P 810675-01-5P 810675-02-6P
     810675-03-7P 810675-19-5P
     RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
     USES (Uses)
        (preparation of biarylbisphosphines as chiral ligands for ruthenium complex
        catalyzed enantioselective hydrogenation or in asym. synthesis)
     810674-60-3 CAPLUS
RN
     Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-
CN
     biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)
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RN 810674-92-1 CAPLUS

CN Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[dicyclohexyl- (9CI) (CA INDEX NAME)

RN 810674-93-2 CAPLUS

CN Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[dicyclohexyl- (9CI) (CA INDEX NAME)

RN 810674-94-3 CAPLUS

Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis[3,5-bis(1,1-dimethylethyl)-4-methoxyphenyl]-(9CI) (CA INDEX NAME)

RN 810674-95-4 CAPLUS

CN Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis[3,5-bis(1,1-dimethylethyl)-4-methoxyphenyl]-(9CI) (CA INDEX NAME)

RN 810674-96-5 CAPLUS CN Phosphine oxide, [(3

Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis(3,5-dimethylphenyl)- (9CI) (CA INDEX NAME)

RN 810674-97-6 CAPLUS
CN Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis(3,5-dimethylphenyl)- (9CI) (CA INDEX NAME)

RN 810674-98-7 CAPLUS

CN Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-methoxy-3,5-dimethylphenyl)- (9CI) (CA INDEX NAME)

RN 810674-99-8 CAPLUS

CN Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-methoxy-3,5-dimethylphenyl)- (9CI) (CA INDEX NAME)

RN 810675-00-4 CAPLUS

CN Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-fluorophenyl)- (9CI) (CA INDEX NAME)

PAGE 3-A

RN 810675-01-5 CAPLUS

CN

Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-fluorophenyl)- (9CI) (CA INDEX NAME)

PAGE 3-A

RN 810675-02-6 CAPLUS
CN Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis[3,5-bis(1,1-dimethylethyl)phenyl]- (9CI) (CA INDEX NAME)

PAGE 2-A

RN 810675-03-7 CAPLUS

Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-bis(2-propenyloxy)[1,1'-biphenyl]-2,2'-diyl]bis[bis[3,5-bis(1,1-dimethylethyl)phenyl]- (9CI) INDEX NAME) CN

PAGE 2-A

RN

810675-19-5 CAPLUS 2-Buten-1-ol, 4,4'-[[(1R)-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-, (2Z,2'Z)- (9CI) (CA INDEX NAME) CN

RN 524711-75-9 CAPLUS
CN [1,1'-Biphenyl]-2,2'-diol, 6,6'-bis(diphenylphosphinyl)-, (1R)- (9CI) (CA INDEX NAME)

RN 810674-62-5 CAPLUS CN 3-Hexen-1-ol, 6,6'-[[(1S)-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-

diyl]bis(oxy)]bis-, (3Z,3'Z)- (9CI) (CA INDEX NAME)

RN 810674-63-6 CAPLUS CN 2-Buten-1-ol, 4,4'-[[(1R)-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-, (2E,2'E)- (9CI) (CA INDEX NAME)

RN 810674-67-0 CAPLUS
CN 1-Propanol, 3,3'-[[(1S)-3,3'-dichloro-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis- (9CI) (CA INDEX NAME)

RN 810674-68-1 CAPLUS
CN 1-Butanol, 4,4'-[[(1S)-3,3'-dichloro-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis- (9CI) (CA INDEX NAME)

RN 810674-69-2 CAPLUS
CN 1-Butanol, 3,3'-[[(1S)-3,3'-dichloro-6,6'-bis(diphenylphosphinyl)[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis- (9CI) (CA INDEX NAME)

L3 ANSWER 15 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN ACCESSION NUMBER: 2004:308392 CAPLUS

DOCUMENT NUMBER: 2004:308392

TITLE: Isomerization of chiral homogeneous o, o'-dihydroxybiphenyl derivatives INVENTOR(S): Arlt, Dieter PATENT ASSIGNEE(S): Germany SOURCE: PCT Int. Appl., 26 pp. CODEN: PIXXD2 DOCUMENT TYPE: Patent LANGUAGE: German FAMILY ACC. NUM. COUNT: PATENT INFORMATION: PATENT NO. APPLICATION NO. KIND DATE DATE -----\_\_\_\_ ----------WO 2003-EP10764 WO 2004031110 A2 20040415 20030927 WO 2004031110 ΑЗ 20040610 AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG 20040422 DE 10324878 A1 DE 2003-10324878 20030602 AU 2003273926 Α1 20040423 AU 2003-273926 20030927 PRIORITY APPLN. INFO.: DE 2002-10246137 A 20021001 DE 2003-10324878 20030602 Α WO 2003-EP10764 20030927 W OTHER SOURCE(S): CASREACT 140:321522; MARPAT 140:321522 Chiral homogeneous o,o'-dihydroxybiphenyl derivs., which either act as bisphosphine ligands of enantioselective transition metal complex catalysts (no data), or are used as intermediate products for producing ligands of this type, can be isomerized by thermal treatment, optionally in the presence of substances with an alkaline action, to produce a mixture of both enantiomers. The inventive method permits the targeted production of a ligand for enantioselective transition metal complex catalysts in (R)- or (S) - form, enabling the undesired enantiomer to be used. Thus, reaction of (R)-(6,6'-dihydroxybiphenyl-2,2'-diyl)bis(diphenylphosphine) with BuLi in ethylene glycol/hexane followed by heating the solution at 160° for 24h and HCl hydrolysis gave a mixture of (R)- and (S)-(6,6'dihydroxybiphenyl-2,2'-diyl)bis(diphenylphosphine). ΙT 185913-95-5P 524711-75-9P 679422-50-5P 691363-03-8P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(isomerization of chiral homogeneous dihydroxybiphenyl phosphine derivs.)

RN 185913-95-5 CAPLUS

CN Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133577-84-1 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 185913-96-6 CAPLUS
CN Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 679002-66-5 CAPLUS
CN [1,1'-Biphenyl]-2,2',3,3'-tetrol, 6,6'-bis(diphenylphosphinyl)- (CA INDEX NAME)

RN 679002-68-7 CAPLUS
CN [1,1'-Biphenyl]-2,2',3,3'-tetrol, 6,6'-bis[bis(3,5-dimethylphenyl)phosphinyl]- (CA INDEX NAME)

RN691363-04-9 CAPLUS

CN [1,1'-Biphenyl]-2,2'-diol, 3,3'-dichloro-6,6'-bis(diphenylphosphinyl)-, (1R) - (9CI) (CA INDEX NAME)

ANSWER 16 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2002:980764 CAPLUS

DOCUMENT NUMBER:

138:376639

TITLE:

(R) - (6, 6'-Dihydroxybiphenyl-2, 2'-

AUTHOR(S):

diyl)bis(diphenylphosphine oxide) methanol solvate Qiu, Li Qin; Qi, Jian Ying; Ji, Jian Xin; Zhou, Zhong

Yuan; Yeung, Chi Hung; Choi, Michael C. K.; Chan,

Albert S. C.

CORPORATE SOURCE:

Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis

and Department of Applied Biology and Chemical

Technology, Hong Kong Polytechnic University, Hong Kong, Peop. Rep. China

SOURCE:

Acta Crystallographica, Section C: Crystal Structure

Communications (2003), C59(1), o33-o35

CODEN: ACSCEE; ISSN: 0108-2701

PUBLISHER:

Blackwell Munksqaard

DOCUMENT TYPE:

Journal

LANGUAGE:

English

The title compound, C36H28O4P2·CH4O, was synthesized directly from the methoxy analog. The crystal structure shows that one OH group interacts with an O atom of a phosphine oxide group in an adjacent mol., while the other OH group complexes with the MeOH solvent mol. via intermol. H bonds. An O atom of one phosphine oxide group interacts with the hydroxy H atom of MeOH via a H bond. There are intra- and intermol.  $\pi\text{-}\pi$  interactions between the Ph rings. All these interactions gave supramol. chiral parallelogram channels via self-assembly. Crystallog. data are given.

ΙT 524711-76-0P, (R) - (6,6'-Dihydroxybiphenyl-2,2'-

CM 2

CRN 67-56-1 CMF C H4 O

 ${\tt H3C-OH}$ 

REFERENCE COUNT:

ANSWER 17 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2002:364020 CAPLUS

DOCUMENT NUMBER:

136:369840

TITLE:

Improved method for the preparation of

enantiomerically pure (5,5'-dichloro-6,6'dimethoxybiphenyl-2,2'-diyl)-bis-(diphenylphosphine

INVENTOR(S):

Pohl, Torsten; Prinz, Thomas; Giffels, Guido; Sirges,

Wolfgram

PATENT ASSIGNEE(S):

Bayer Aktiengesellschaft, Germany

SOURCE:

Eur. Pat. Appl., 12 pp.

CODEN: EPXXDW

DOCUMENT TYPE: LANGUAGE:

Patent German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

	PATENT NO.						KIND DATE			PLIC	DATE					
	EP 1205486			A1	200	EP	EP 2001-126101						20011102			
	EΡ	1205486			В1	B1 20040211 ·			•							
		R:	AT,	BE,	CH,	DE,	DK, ES	, FR,	GB, G	R, I'	T, LI	, LU,	NL,	SE,	MC,	PT,
			ΙE,	SI,	LT,	LV,	FI, RO	, MK,	CY, A	L, T	R					
	DE	1005	6310			A1	200	20516	DE	200	0-100	56310		2	0001	114
	ΑT	2593	71			${f T}$	200	40215	AT	200	1-126	101		2	0011	102
	ES	2215	835			Т3	200	41016	ES	200	1-126	101		2	0011	102
	JP,	2002	1796	93		Α	200	20626	JP	200	1-343	031		2	0011	108
	JΡ	3900	254			В2	200	70404								
	US	2002	00588	814		A1	200	20516	US	200	1-101	76		2	0011	113
	US	6489	513			В2	200	21203								
PRIOR	ITY	APP	LN.	INFO	.:				DE	200	0-100	56310	7	A 2	0001	114
OTHER	SC	URCE	(S):			CASI	REACT 1	36:36	9840							

The preparation of title compound is described in four steps starting from 5-bromo-2-chloroanisole. Thus, phosphination of 5-bromo-2-chloroanisole with diphenylphosphinic chloride in presence of Mg in THF gave 82% (4-chloro-3-methoxyphenyl)diphenylphosphine oxide which on lithiation with LDA followed by iodination in THF gave 93.5% (4-chloro-2-iodo-3methoxyphenyl)diphenylphosphine oxide. Copper-mediated coupling of (4-chloro-2-iodo-3-methoxyphenyl)diphenylphosphine oxide in PhMe followed by resolution with (+)-dibenzoyltartaric acid and reduction with HSiCl3 in xylene

gave enantiomerically pure title compound, (5,5'-dichloro-6,6'dimethoxybiphenyl-2,2'-diyl)-bis-(diphenylphosphine oxide).

ΙT 185913-96-6P

> RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of)

RN 185913-96-6 CAPLUS

CN Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-dimethoxy[1,1'-biphenyl]-2,2'diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

L3 ANSWER 18 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2001:880027 CAPLUS

DOCUMENT NUMBER: 136:166979

TITLE: Disparate Roles of Chiral Ligands and Molecularly

Imprinted Cavities in Asymmetric Catalysis and Chiral

Poisoning

AUTHOR(S): Koh, Jeong Hwan; Larsen, Andrew O.; White, Peter S.;

Gagne, Michel R.

CORPORATE SOURCE: Department of Chemistry, University of North Carolina,

Chapel Hill, NC, 27599-3290, USA

SOURCE: Organometallics (2002), 21(1), 7-9 CODEN: ORGND7; ISSN: 0276-7333

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 136:166979

Ι

GΙ

AB The activation of molecularly imprinted metal complexes generated Lewis acid catalysts, prepared via copolymn. of metallomonomers (I; X = C1, X2 = O,O-dideprotonated (S)-, (R)-BINOL; Ar = p-C6H4C(CH3):CH2) with EDMA (ethylene dimethacrylate), for the ene reaction, each of which contains a chiral diphosphine ligand and a chiral BINOL-shaped cavity. Poisoning expts. with (R) - and (S) -BINAM (where (R) - and (S) -BINAM = (R) - and (S)-1,1'-binaphthyl-2,2'-diamine, resp.) indicated that while the chiral cavity can differentiate the chiral poisons, it is the chiral diphosphine ligand which controls the enantioselectivity of the ene product.

ΙT 145265-38-9

> RL: RCT (Reactant); RACT (Reactant or reagent) (lithium aluminum hydride reduction of)

RN 145265-38-9 CAPLUS

Phosphonic acid, P,P'-[(1S)-2',6-dimethoxy[1,1'-biphenyl]-2,6'-diyl]bis-, CN P, P, P', P'-tetraethyl ester (CA INDEX NAME)

REFERENCE COUNT:

L3 ANSWER 19 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2001:228894 CAPLUS

DOCUMENT NUMBER: 134:266437

TITLE: Chiral phosphines, transition metal complexes thereof

and uses thereof in asymmetric reactions

INVENTOR(S): Zhang, Xumu

PATENT ASSIGNEE(S): Penn State Research Foundation, USA

SOURCE: PCT Int. Appl., 52 pp.

CODEN: PIXXD2

DOCUMENT TYPE:

Patent

LANGUAGE:

English

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

P.	PATENT NO.				KIND DATE			APPLICATION NO.					DATE				
. Mo	2001	0216	25		A1		2001	0329		WO 2	2000-	US25	635		2	0000	919
											BG,						
		CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EE,	ES,	FI,	GB,	GD,	GE,	GH,	GM,	HR,
		HU,	ID,	IL,	IN,	IS,	JP,	KE,	KG,	ΚP,	KR,	ΚZ,	LC,	LK,	LR,	LS,	LT,
		LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NO,	NZ,	PL,	PT,	RO,	RU,
		SD,	SE,	SG,	SI,	SK,	SL,	ТJ,	TM,	TR,	TT,	TZ,	UA,	UG,	US,	UZ,	VN,
		YU,	ZA,	ZW													
	RW:	GH,	GM,	KE,	LS,	MW,	MZ,	SD,	SL,	SZ,	ΤZ,	UG,	ZW,	AT,	BE,	CH,	CY,
		DE,	DK,	ES,	FI,	FR,	GB,	GR,	ΙE,	IT,	LU,	MC,	NL,	PT,	SE,	BF,	ВJ,
		CF,									NE,						
	CA 2385421				A1		2001	0329	CA 2000-2385421						2	0000	919
	P 1214									EP 2	2000-	9651	36		2	0000	919
E.	P 1214										<u>~</u>						
	R:										IT,	LI,	LU,	NL,	SE,	MC,	PT,
							RO,										
	S 6521	.769			В1		2003	0218		US 2	2000-	6654	56		2	0000	919
J	P 2003 T 3249	35095	13		T		2003	0311		JP 2	2001-	5250	00		2	0000	
A'	Г 3249	943			T		2006	0615		AT 2	2000-	9651	36		2	0000	
	S 2263				Т3		2006	1216								0000	
PRIORI'	PRIORITY APPLN. INFO.:									999-							
											2000-				W 2	0000	919
OTHER :	SOURCE	E(S):			CAS	REAC	T 13	4:26	6437	; MA	ARPAT	134	:266	437			

Ι

AΒ Chiral ligands and transition metal complexes based on such chiral ligands useful in asym. catalysis are disclosed. The chiral ligands include chiral C1-C6-TunaPhos ligands I (n = 1-6). The ruthenium TunaPhos complex reduces ketones to the corresponding alcs. with 95-99.6 % enantioselectivity. The transition metal complexes of the chiral ligands are useful in asym. reactions such as asym. hydrogenation, hydride transfer, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, hydrocarboxylation, isomerization, allylic alkylation, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization,

Aldol reaction, Michael addition and epoxidn. reactions.

IT 133577-82-9, (R)-(6,6'-Dimethoxybiphenyl-2,2'-

diyl)bis(diphenylphosphine oxide)

RL: RCT (Reactant); RACT (Reactant or reagent)

(reduction of)

RN 133577-82-9 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 20 OF 31 CAPLUS' COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

2001:28618 CAPLUS

DOCUMENT NUMBER:

134:86384

TITLE:

Process for the racemization of atropisomeric

bis (phosphine oxide) compounds

INVENTOR(S):

Kienzle, Frank; Lalonde, Michel; Schmid, Rudolf; Wang,

Shaoning

PATENT ASSIGNEE(S):

F. Hoffmann-La Roche A.-G., Switz.

SOURCE:

Eur. Pat. Appl., 12 pp. CODEN: EPXXDW

DOCUMENT TYPE:

Patent

LANGUAGE:

English

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND DATE		APPLICATION NO.	DATE		
EP 1067133 EP 1067133	A1 B1	20010110	EP 2000-114219	20000703		
R: AT, BE, CH, IE, SI, LT,	DE, DK	, ES, FR,	GB, GR, IT, LI, LU, NL,	SE, MC, PT,		
US 6288280	в1	20010911	US 2000-594643	20000615		
AT 250072	Т	20031015	AT 2000-114219	20000703		
ES 2204411	Т3	20040501	ES 2000-114219	20000703		
CA 2313338	A1	20010109	CA 2000-2313338	20000704		
JP 2001039993	A	20010213	JP 2000-203499	20000705		
JP 3688563	B2	20050831				
IN 2000MA00517	A	20070420	IN 2000-MA517	20000705		
CN 1281860	A	20010131	CN 2000-120417	20000707		
BR 2000002650	A	20010313	BR 2000-2650	20000707		
MX 2000PA06740	Α	20050414	MX 2000-PA6740	20000707		
PRIORITY APPLN. INFO.:				A 19990709		
OTHER SOURCE(S):	MARPAT	134:86384				
GI						

The present invention is concerned with a novel process for the racemization of atropisomeric bis(phosphine oxide) compds. I (R1 = C1-8 alkoxy, R2 = H, C1-8 alkyl, C1-8 alkoxy, R1R2 = methylenedioxy, ethylenedioxy; R3 = H, C1-8 alkyl, C1-8 alkoxy; R4 = (un)substituted Ph) in their (S) or (R) or non-racemic form, for the preparation of optical active bisphosphine ligands, which form optical active complexes with transition metals are formed. These complexes are used as catalysts in a number of asym. reactions. The racemization is thermal and carried out in high or low boiling solvent, under normal or elevated pressure at 105 to 3.5x107 Pa. The heating is performed in a system which allows heating up to 400° (reactor, autoclave, aluminum block, round-bottom flask with heating/stirring mantle and the like) or by microwave irradiation or in the melt at a temperature from 260-400°, preferably from 280-380°, batchwise or in a continuous manner.

IT 133545-15-0P, (RS)-MeOBIPHEPO 133545-18-3P, (RS)-DiMeOBIPHEPO 133545-23-0P, (RS)-p-Tol-MeOBIPHEPO RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)

RN 133545-15-0 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-diphenyl- (CA INDEX NAME)

RN 133545-18-3 CAPLUS

Phosphine oxide, (5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133545-23-0 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)

PAGE 1-A

PAGE 2-A

IT 133577-82-9, (R)-MeOBIPHEPO 133577-84-1, (S)-MeOBIPHEPO
 133577-86-3, (S)-DiMeOBIPHEPO 133577-87-4,
 (R)-DiMeOBIPHEPO 133577-89-6, (S)-p-Tol-MeOBIPHEPO
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (thermal or microwave irradiation racemization of)
RN 133577-82-9 CAPLUS
CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-bipheny]]-2

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN: 133577-84-1 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-86-3 CAPLUS
CN Phosphine oxide, [(1S)-5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133577-87-4 CAPLUS

CN Phosphine oxide, [(1R)-5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133577-89-6 CAPLUS

CN Phosphine oxide, [(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)

REFERENCE COUNT:

THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 21 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN ACCESSION NUMBER: 2000:574233 CAPLUS

3

DOCUMENT NUMBER:

133:309942

TITLE:

SOURCE:

PUBLISHER:

LANGUAGE:

Synthesis of Chiral Bisphosphines with Tunable Bite

Angles and Their Applications in Asymmetric

Hydrogenation of  $\beta$ -Ketoesters

AUTHOR(S):

CORPORATE SOURCE:

Zhang, Zhaoguo; Qian, Hu; Longmire, James; Zhang, Xumu Department of Chemistry, The Pennsylvania State

University, University Park, PA, 16802, USA Journal of Organic Chemistry (2000), 65(19), 6223-6226

CODEN: JOCEAH; ISSN: 0022-3263

American Chemical Society

Journal

English

OTHER SOURCE(S):

DOCUMENT TYPE:

GI

CASREACT 133:309942

Ι

A series of chiral bisphosphines I (n = 1-6) with tunable dihedral angles AΒ were prepared for the first time and used for Ru-catalyzed asym. hydrogenation of  $\beta$ -ketoesters. Enantioselectivities with the Ru-I (n = 4) catalyst are comparable or better than those observed with Ru-BINAP and Ru-MeO-BIPHEP complexes, while enantioselectivities in asym. hydrogenation of  $\beta$ -ketoesters are low with other catalysts e.g., Ru-I (n = 1, 6). The current study demonstrates the concept that changes in ligand dihedral angles indeed cause significant variations of enantioselectivity.

IT 133577-82-9

RL: RCT (Reactant); RACT (Reactant or reagent) (reduction of)

133577-82-9 CAPLUS RN

Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-dCN diyl]bis[1,1-diphenyl- (CA INDEX NAME)

REFERENCE COUNT:

ANSWER 22 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN L3

ACCESSION NUMBER:

2000:37891 CAPLUS

DOCUMENT NUMBER:

132:93468

TITLE:

Preparation of biphenyl diphosphine oxide by

lithiation and oxidative coupling of phenylphosphine

oxide

INVENTOR(S):

Yokozawa, Susumu; Saito, Takao; Sayo, Noboru;

Ishizaki, Takeo

PATENT ASSIGNEE(S):

Takasago Perfumery Co., Ltd., Japan

SOURCE:

Jpn. Kokai Tokkyo Koho, 14 pp.

CODEN: JKXXAF

DOCUMENT TYPE:

Patent

LANGUAGE:

Japanese

FAMILY ACC. NUM. COUNT:

1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2000016997	Α	20000118	JP 1998-181027	19980626
JP 3146187	В2	20010312		
PRIORITY APPLN. INFO.:			JP 1998-181027	19980626
OTHER SOURCE(S):	CASREA	ACT 132:9346	8; MARPAT 132:93468	
CT				

$$\mathbb{R}^3$$
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 $\mathbb{R}^6$ 

Ι

AΒ The title compds. [I; R1 = cycloalkyl, (un) substituted Ph, naphthyl, pyridyl, quinolyl, isoquinolyl, furfuryl, benzofurfuryl, thienyl, or benzothienyl; R2 = lower alkyl, lower ether, lower haloalkyl, Ph; X = hetero atom; R3, R4 = hydrogen, halogen, lower alkyl, lower alkoxy, di(lower alkyl)amino, lower haloalkyl, Ph; or R2 and R2 or R3 and R4 are linked to each other to form a ring] are prepared by treatment of phosphine oxide (II; R1 - R4, X = same as above) with base followed by dimerization using oxidizing agent. I are useful as intermediates for diphosphine compds. which are ligands of metal coordination compds. for an synthesis catalyst. Thus, a solution of 75.22 g diphenyl(3,4methylenedioxyphenyl)phosphine oxide in 300 mL THF was added dropwise at -10° to -5° to a solution of lithium disopropylamide prepared by treatment of 40 mL diisopropylamine in THF with 175 mL 1.7 M BuLi solution and stirred at -12° for 15 min to give a lithium reagent which was added to 5.79 g FeCl3 in 150 mL toluene and 150 mL THF under ice-cooling at 8-10° over 30 min and stirred at room temperature overnight to give 74.8% biphenyl bisphosphine oxide (III). 133545-15-0P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of biphenyl diphosphine oxide by lithiation and oxidative coupling of phenylphosphine oxide)

RN 133545-15-0 CAPLUS

> Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1diphenyl- (CA INDEX NAME)

ANSWER 23 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

1999:425600 CAPLUS

DOCUMENT NUMBER:

131:44958

TITLE:

ΙT

CN

Process for the manufacture of bis(phosphine oxide)

and bis(phosphonate) compounds

INVENTOR(S):

Foricher, Joseph; Schmid, Rudolf F. Hoffmann-La Roche A.-G., Switz.

PATENT ASSIGNEE(S): SOURCE:

Eur. Pat. Appl., 17 pp.

CODEN: EPXXDW

DOCUMENT TYPE:

Patent English

LANGUAGE:

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT	NO.	KIND	DATE	APPLICATION NO.		DATE		
EP 9261 EP 9261		A1 B1	19990630 20020911	EP 1998-123996		19981217		
R:	AT, BE, CH, IE, SI, LT,	DE, DK		GB, GR, IT, LI, LU, N	L, S	E, MC, PT,		
US 6162		A	20001219	US 1998-212646		19981215		
AT 2239	23	T	20020915	AT 1998-123996		19981217		
ES 2182	211	Т3	20030301	ES 1998-123996		19981217		
CA 2256	828	A1	19990623	CA 1998-2256828		19981218		
JP 1124	6576	Α	19990914	JP 1998-364044		19981222		
CN 1224	019	Α	19990728	CN 1998-125786		19981223		
CN 1132	839	В	20031231					
PRIORITY APE	LN. INFO.:			EP 1997-122720	Α	19971223		
				EP 1998-123996	Α	19981217		
OTHER SOURCE	(S):	CASREA	CT 131:449	958; MARPAT 131:44958				

GΙ

$$R^{2}$$
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 $R^{2}$ 
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 $R^{5}$ 
 $R^{5}$ 
 $R^{6}$ 
 $R^{6$ 

II

Ι

AB A process for the manufacture of bisphosphine oxide compds. I and II (R1, R2 = H, C1-8 alkyl, (un)substituted Ph, C1-8 alkoxy, phenyloxy, benzyloxy, halo, di-C1-8 alkylamino; R1R2 = fused ring, etc.; R3, R5 = H, C1-8 alkyl, (un)substituted Ph, C1-8 alkoxy, (un)substituted phenyloxy, benzyloxy, halo, di-C1-8 alkylamino; R4 = C1-8 alkoxy, (un)substituted phenyloxy, C1-8 alkyl, C3-7 cycloalkyl, (un)substituted Ph, naphthyl, heteroaryl, etc.; X = O, S) and bisphosphonates as intermediates for the production of bisphosphine ligands, in which in a single step process (a) a phosphine oxide compound is reacted in an organic solvent at -70°-20° with 0.5-3 equivalent of a lithium or magnesium amide compound, (b) 0.5-3 equivalent of

oxidatively-acting metal salt or metal salt complex are added to the mixture obtained in stage (a) in a temperature range of  $-70^{\circ}-20^{\circ}$ , with a racemate of a bisphosphine oxide compound being obtained; (c) a racemate cleavage is carried out if desired; and (d) the bisphosphonates obtained in stage (b) or (c) are converted into bisphosphine oxides. Thus, Grignard reaction of 3-bromoanisole with P-chlorodiphenylphosphine in THF followed by H2O2 oxidation gave 88.8% (3-methoxyphenyl)diphenylphosphine oxide. Coupling reaction of (3-methoxyphenyl)diphenylphosphine oxide in the presence of FeCl3 gave title compound I (R1 = OMe, R2, R3 = H, R4 = Ph).

IT 133545-15-0P 133545-18-3P 145209-14-9P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)

RN 133545-15-0 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-diphenyl- (CA INDEX NAME) .

RN 133545-18-3 CAPLUS

CN Phosphine oxide, (5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenyl- (9CI) (CA INDEX NAME)

RN 145209-14-9 CAPLUS

CN Phosphonic acid, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, P,P,P',P'-tetraethyl ester (CA INDEX NAME)

REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 24 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1999:348800 CAPLUS

DOCUMENT NUMBER: 131:102342

TITLE: Synthesis and use of water-soluble sulfonated

dibenzofuran-based phosphine ligands

AUTHOR(S): Gelpke, Arjan E. Sollewijn; Veerman, Johan J. N.;

Goedheijt, Marcel Schreuder; Kamer, Paul C. J.; Van

Leeuwen, Piet W. N. M.; Hiemstra, Henk

CORPORATE SOURCE: Laboratories of Inorganic and Organic Chemistry,

Institute of Molecular Chemistry, University of

Amsterdam, Amsterdam, 1018 WS, Neth.

SOURCE: Tetrahedron (1999), 55(21), 6657-6670

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Science Ltd.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 131:102342

The syntheses of three triphenylphosphine analogs with one, two or three Ph groups replaced by 2-dibenzofuranyl groups, resp., and one enantiopure analog of the atropisomeric diphosphine MeO-BIPHEP with all four Ph groups replaced by 2-dibenzofuranyl are reported. Sulfonation of these compds. with sulfuric acid at room temperature proceeded with complete regioselectivity at the 8-position in the dibenzofuran moieties. These results proved the usefulness of dibenzofuran as a structural moiety in the synthesis of water-soluble phosphine ligands. The dibenzofuran-based, water-soluble triphenylphosphine analogs were used as ligands in palladium-catalyzed aqueous phase Heck and Suzuki reactions and in the rhodium-catalyzed two-phase hydroformylation of propene.

IT 145209-12-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

CM 1 CRN 230635-53-7 CMF C62 H40 O8 P2

CM 2
CRN 138794-81-7
CMF C18 H18 O6

Absolute stereochemistry. Rotation (-).

IT 230635-56-0DP, complex 230635-57-1DP, complex
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
(Reactant or reagent)

(preparation and hydrolysis of)

RN 230635-56-0 CAPLUS

CN Butanedioic acid, 2,3-bis(phenylmethoxy)-, (2R,3R)-, compd. with [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[di-2-dibenzofuranylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 230635-55-9 CMF C62 H40 O8 P2

CM 2

CRN 138794-81-7 CMF C18 H18 O6

Absolute stereochemistry. Rotation (-).

RN 230635-57-1 CAPLUS

CN Butanedioic acid, 2,3-bis(phenylmethoxy)-, (2S,3S)-, compd. with [(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[di-2-dibenzofuranylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 2

CRN 116679-01-7 CMF C18 H18 O6

Absolute stereochemistry. Rotation (+).

IT 230310-72-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and optical resolution of)

RN 230310-72-2 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(2-dibenzofuranyl)- (9CI) (CA INDEX NAME)

PAGE 2-A

IT 230635-53-7P 230635-55-9P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(preparation as cocatalyst for Heck and Suzuki reaction and hydroformylation of propene)

RN 230635-53-7 CAPLUS

CN Phosphine oxide, [(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[di-2-dibenzofuranyl- (9CI) (CA INDEX NAME)

RN 230635-55-9 CAPLUS

CN Phosphine oxide, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[di-2-dibenzofuranyl- (9CI) (CA INDEX NAME)

REFERENCE COUNT:

51 THERE ARE 51 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 25 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

1997:94054 CAPLUS

DOCUMENT NUMBER:

126:104246

TITLE:

Preparation of enantiomerically pure bisphosphines and use of their Group VIII metal complexes as catalysts

for asymmetric hydrogenation

INVENTOR(S):

Laue, Christian; Schroeder, Georg; Arlt, Dieter

PATENT ASSIGNEE(S):

Bayer A.-G., Germany Eur. Pat. Appl., 13 pp.

CODEN: EPXXDW

DOCUMENT TYPE:

Patent

LANGUAGE:

SOURCE:

German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE		
EP 749973	A1	19961227	EP 1996-109252	19960610		
EP 749973	В1	20011114				

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LI, LU, MC, NL, PT, SE

DE 19522293		A1	19970102	DE	1995-19522293		19950620
AT 208782		T	20011115.	AT	1996-109252		19960610
PT 749973		T	20020429	PT	1996-109252		19960610
ES 2167489		T3	20020516	ES	1996-109252		19960610
US 5710339		A	19980120	US	1996-664073		19960613
TW 427994		В	20010401	TW	1996-85107135		19960614
CA 2179244		A1	19961221	CA	1996-2179244		19960617
CA 2179244		С	20060822				
JP 09003082		Α	19970107	JP	1996-175446		19960617
JP 3862784		B2	20061227				
IL 118670		Α	20000726	IL	1996-118670		19960617
HU 9601699		A2	19970428	HU	1996-1699		19960620
HU 9601699		A3	19970828		•		
HU 215283		В	19981130				
US 5801261		A	19980901	US	1997-953473		19971017
PRIORITY APPLN. INFO	).:			DE	1995-19522293	Α	19950620
				US	1996-664073	A1	19960613

OTHER SOURCE(S):

CASREACT 126:104246; MARPAT 126:104246

$$\begin{array}{c|c} \text{Cl} & & \\ \text{Me} & & \\ \text{Me} & & \\ \text{P} & \\ \text{R} & \\ \end{array}$$

Ι

AB Enantiomers of I, a procedure for their preparation, their use to make Group VIII metal complexes, and use of the complexes as asym. hydrogenation catalysts are claimed. In I, R = Ph with optionally 1-3 substituents = OR1, R1, nitro, NH2, NHR1, NR12 (R1 = C2-6 alkyl), C2-7 alkyl, or C3-7 cycloalkyl. For example, I (R = Ph) was prepared via the following steps: a Grignard reaction of 5-bromo-2-chloroanisole with Ph2P(O)Cl gave diphenyl(4-chloro-3-methoxyphenyl)phosphine oxide, which was iodinated at the 2 position; coupling of the iodinated derivative using Cu/DMF gave the racemic P,P-dioxide of I, which was resolved by fractional crystallization using

(-)-dibenzoyltartaric acid; the phosphine oxide enantiomers were then reduced by Cl3SiH in xylene/Bu3N to give the enantiomers of I. Examples show how Ru complexes of one of the enantiomers catalyzed hydrogenation of 2-(3-benzylphenyl)propenoic acid with 88% enantiomeric excess (ee) and of Me acetate with 97% ee.

IT 185836-54-8P

CN

RL: PEP (Physical, engineering or chemical process); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)

(preparation of enantiomerically pure bisphosphines and use of Group VIII metal complexes as catalysts for asym. hydrogenation)

RN 185836-54-8 CAPLUS

Phosphine oxide, [3',5-dichloro-6'-(diphenylphosphinyl)-2',6-dimethoxy[1,1'-biphenyl]-2-yl]diphenyl- (CA INDEX NAME)

CN

IT 185913-95-5P 185913-96-6P RL: PUR (Purification or recovery); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation of enantiomerically pure bisphosphines and use of Group VIII metal complexes as catalysts for asym. hydrogenation) RN 185913-95-5 CAPLUS Phosphine oxide, [(1S)-5,5'-dichloro-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-

Ph Ph Ph. Cl OMe OMe

diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 185913-96-6 CAPLUS Phosphine oxide, [(1R)-5,5'-dichloro-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-CN diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

ANSWER 26 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN L3 ACCESSION NUMBER: 1994:298626 CAPLUS

DOCUMENT NUMBER: 120:298626 TITLE:

Asymmetric hydrogenation with optically active

ruthenium diphosphine catalysts and application to a

cilazapril intermediate

INVENTOR(S):

Broger, Emil Albin; Crameri, Yvo; Imfeld, Marquard;

Montavon, Francois; Widmer, Erich

PATENT ASSIGNEE(S):

F. Hoffmann-La Roche & Co. AG, Switz.

SOURCE:

Eur. Pat. Appl., 18 pp.

CODEN: EPXXDW

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.		DATE
EP 570764	A2	19931124	EP 1993-107272		19930505
EP 570764	A3	19940629			
EP 570764	B1	20010718			
R: AT, BE, CH,	DE, DK	, ES, FR, GB	, IT, LI, NL		
AT 203242	${f T}$	20010815	AT 1993-107272		19930505
ES 2164056	Т3	20020216	ES 1993-107272		19930505
JP 06032780	Α	19940208	JP 1993-114776		19930517
JP 3526310	B2	20040510			
US 5750690	Α	19980512	US 1996-690215 ·		19960726
PRIORITY APPLN. INFO.:			CH 1992-1582	Α	19920518
			CH 1993-729	Α	19930311
		÷	US 1993-57231	В1	19930504
			US 1994-330404	В1	19941028
OTHER SOURCE(S):	CASREA	CT 120:29862	6; MARPAT 120:298626		

CO2H

GI

Ι

CO2H

(R) - or (S) -stereoisomers of heterocycles I [R = alkyl, arylmethyl, aryl, ...]AR alkoxy, arylmethoxy, aryloxy; or RR = CH2, CH2CH2, 1,2-C6H4; n = 1, 2, 3] are prepared by asym. hydrogenation of corresponding unsatd. heterocycles II or their salts in the presence of optically active Ru diphosphine complexes as catalysts. Addnl. claims specify the diphosphines, and the example product and reactant given below, and cover starting materials and their preparation For example, hydrogenation of the tetrahydropyridazinophthalazine II (RR = 1,2-C6H4, n = 2) in MeOH containing Et3N and the complex Ru(OAc)2[(S)-p-TolMeOBIPHEP] [cited ligand = (S)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis[di-(p-tolyl)phosphine]] at 60° and 40 bar gave 100% conversion in 1 h. Workup and acidic precipitation of product gave (S)-I (RR = 1,2-C6H4, n = 2) [(S)-III], an intermediate for the antihypertensive cilazapril, in 96% yield and 98.9% optical purity. Addnl. similar catalysts gave 85-95% yield and 97.3-98.9% optical purity for the same reaction. Addnl. examples include analogous preparation of (R)-III, and prepns. of the starting material. IT 145265-37-8

II

RL: RCT (Reactant); RACT (Reactant or reagent) (Grignard reaction of, in preparation of ligand for ruthenium hydrogenation catalysts)

RN 145265-37-8 CAPLUS

CN Phosphonic acid, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, tetraphenyl ester, (S)- (9CI) (CA INDEX NAME)

ΙT 150971-42-9P

> RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of, in preparation of ligand for ruthenium catalysts)

RN 150971-42-9 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(1methylethyl)-, (S)- (9CI) (CA INDEX NAME)

ANSWER 27 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1993:671399 CAPLUS

DOCUMENT NUMBER:

.119:271399

TITLE: Preparation of racemic and optically active

> diphosphine ligands for use in ruthenium asymmetric hydrogenation catalysts for prochiral allylic systems

INVENTOR(S):

Foricher, Joseph; Schmid, Rudolf Hoffmann-La Roche, F., und Co. A.-G., Switz. PATENT ASSIGNEE(S):

SOURCE: PCT Int. Appl., 19 pp.

CODEN: PIXXD2

DOCUMENT TYPE:

Patent LANGUAGE: German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9315091 W: JP. US	A1	19930805	WO 1993-CH26	19930201

RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

	579797			A1	19940126	EP 1993-902021		19930201
EP	579797			В1	19990421			
		BE,	CH,			GB, IT, LI, NL		
	06506475			$\mathbf{T}$		JP 1993-506424		19930201
JP	3369558			B2	20030120			
AT	179981			$\mathbf{T}$		AT 1993-902020	,	19930201
AT	179176			${f T}$		AT 1993-902021		19930201
ES	2131575			т3		ES 1993-902021		19930201
ES	2132215			Т3	19990816	ES 1993-902020		19930201
EP	565975			A2	19931020	EP 1993-105548		19930403
EP	565975			А3	19931103			
EP	565975			В1	19960904			
	R: AT,	BE,	CH,	DE,	DK, ES, FR,	GB, IT, LI, NL		
AT	142191			T	19960915	AT 1993-105548		19930403
ES	2091509			т3	19961101	ES 1993-105548		19930403
JP	06025035			Α	19940201	JP 1993-109833		19930414
JP	3310381			B2	20020805			
US	5457219			Α	19951010	US 1993-122488		19930927
US	5514805			Α	19960507	US 1994-225408		19940408
US	5600015			Α	19970204	US 1995-445068		19950519
US	5750690			Α	19980512	US 1996-690215		19960726
PRIORITY	Y APPLN.	INFO	. :			CH 1992-289	Α	19920131
						CH 1992-1270	Α	19920416
						CH 1992-1582	Α	19920518
						CH 1992-1944	Α	19920619
						US 1993-10120	В1	19930128
						WO 1993-CH26	W	19930201
						CH 1993-729	Α	19930311
						US 1993-44519	В1	19930408
						US 1993-57231	В1	19930504
						US 1994-203859	В1	19940301
						US 1994-330404	В1	19941028
				~ ~ ~ ~	110 02	US 1994-330404		19941028

OTHER SOURCE(S):

CASREACT 119:271399; MARPAT 119:271399

150971-58-7P

Described are racemic optically active phosphorus compds. of the formula AΒ I, in which R is a lower alkyl or lower alkoxy group and Rl is a lower alkyl, cycloalkyl or substituted Ph group. The compds. of the formula I act, in the form of complexes with a group (IV) metal, i.e.,  $di(\eta 2-acetato)(\eta 4-1,5-cyclooctadiene)$ ruthenium (II) (II), as catalysts for asym. hydrogenation reactions and enantiomer-selective hydrogen displacement reactions in prochiral allylic systems. E.g., hydrogenation of 3,4,6,11-tetrahydro-6,11-dioxopyridazo[1,2a]phthalazine-1carboxylic acid by treatment with H2 and II and [(S)-6,6'dimethoxybiphenyl-2,2'-diyl]bis[diisopropylphosphine] gave (S)-1,2,3,4,6,11-hexahydro-6,11-dioxopyridazo[1,2b]phthalazine-1carboxylic acid in 96% yield. IT 145209-28-5P 145209-29-6P 150971-32-7P 150971-34-9P 150971-36-1P 150971-38-3P 150971-40-7P 150971-42-9P 150971-44-1P

150971-46-3P 150971-48-5P 150971-50-9P 150971-52-1P 150971-54-3P 150971-56-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of, ligand for metal catalyst of asym. hydrogenation

reaction by)

145209-28-5 CAPLUS

RN CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis([1,1'biphenyl]-4-yl)-, (R)- (9CI) (CA INDEX NAME)

RN 145209-29-6 CAPLUS

Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis([1,1'-CN biphenyl]-4-yl)-, (S)- (9CI) (CA INDEX NAME)

150971-32-7 CAPLUS

RN

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'diyl)bis[bis([1,1':3',1''-terphenyl]-5'-yl)-, (S)-(9CI)] (CA INDEX NAME)

PAGE 2-A

RN 150971-34-9 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis[3,5-bis(trimethylsilyl)phenyl]-, (R)- (9CI) (CA INDEX NAME)

PAGE 1-A

RN 150971-36-1 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis[3,5-bis(trimethylsilyl)phenyl]-, (S)- (9CI) (CA INDEX NAME)

PAGE 1-A

PAGE 2-A

RN 150971-38-3 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis[3,5-bis(triethylsilyl)phenyl]-, (R)- (9CI) (CA INDEX NAME)

PAGE 2-A

RN 150971-40-7 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis[3,5-bis(triethylsilyl)phenyl]-, (S)- (9CI) (CA INDEX NAME)

PAGE 1-A

RN 150971-42-9 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(1-methylethyl)-, (S)- (9CI) (CA INDEX NAME)

RN 150971-44-1 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(1-methylethyl)-, (R)- (9CI) (CA INDEX NAME)

RN 150971-46-3 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diethyl-(9CI) (CA INDEX NAME)

RN 150971-48-5 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[dicyclobutyl-, (R)- (9CI) (CA INDEX NAME)

RN 150971-50-9 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[dicyclobutyl-, (S)- (9CI) (CA INDEX NAME)

RN 150971-52-1 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[dicyclopentyl-, (R)- (9CI) (CA INDEX NAME)

RN 150971-54-3 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[dicyclopentyl-, (S)- (9CI) (CA INDEX NAME)

RN 150971-56-5 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis([1,1':3',1''-terphenyl]-5'-yl)-, (R)- (9CI) (CA INDEX NAME)

PAGE 1-A

RN 150971-58-7 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis[4-(trimethylsilyl)phenyl]-, (R)- (9CI) (CA INDEX NAME)

IT 145209-12-7 145265-39-0

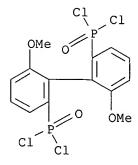
RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with biphenyl Grignard reagent)

RN 145209-12-7 CAPLUS

CN Phosphonic acid, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, tetraphenyl ester (9CI) (CA INDEX NAME)

RN 145265-39-0 CAPLUS

CN Phosphonic dichloride, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis-(9CI) (CA INDEX NAME)



L3 ANSWER 28 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1993:147774 CAPLUS

DOCUMENT NUMBER: 118:147774

TITLE: Preparation and resolution of biphenyl-1,1'-

diphosphonates

INVENTOR(S): Foricher, Joseph; Heiser, Bernd; Schmid, Rudolf

PATENT ASSIGNEE(S): Hoffmann-La Roche, F., und Co. A.-G., Switz.

SOURCE: PCT Int. Appl., 25 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PF	PATENT NO.					KIND DATE		APPLICATION NO.					DATE		
WC	9216				A1	19	921001	WO	1992-	CH50				19920312	
	RW:			CH,	DE, I			GB, GI					SE	E	
EF	5303	35			A1	19	930310	EP	1992-	9052	78			19920312	
E	5303	35			B1 .	19	960814								
	R:	AT,	BE,	CH,	DE, I	K, F	R, GB,	IT, L	I, NL,	SE					
JE	0550	7503			T	19	931028	JP	1992-	5059	15			19920312	
JE	3204	668			B2	20	010904								
ΑT	1412	78			T	19	960815	AT	1992-	9052	78			19920312	
US	5302	738			Α	19	940412	US	1992-	9498	78			19921113	
PRIORIT	Y APP	LN.	INFO	. :				CH	1991-	794		1	A	19910315	
								WO	1992-	CH50		1	N	19920312	
OTHER S	OURCE	(S):			MARPA	T 11	3:1477	74							

GΙ

Title compds. (I; R = alkyl, alkoxy, protected OH; R1 = alkoxy, PhO, AΒ PhCH2O, C1, Br; R2 = alkyl, alkoxy; n = 0-2), were prepared Thus, di-Ph 2-iodo-3-(methoxyphenyl)phosphonate (preparation from 3-bromoanisole given) was heated with activated Cu powder in DMF at 140° to give di-Ph RS-(6,6'-dimethoxybiphenyl-2,2'-diyl)bisphosphonate (RS-II). II was treated with (-)-0,0'-dibenzoyl-L-tartaric acid (III) in CH2Cl2/EtOAc to give (R)-II.III, which in CH2Cl2 was stirred with NaHCO3 in H2O to give (R)-II.

IT 145306-47-4P 145306-48-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and decomposition reaction of)

RN 145306-47-4 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [R-(R\*,R\*)]-, compd. with (R)-tetraphenyl (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[phosphonate] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 145265-36-7 CMF C38 H32 O8 P2

CM 2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 145306-48-5 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [S-(R\*,R\*)]-, compd. with (S)-tetraphenyl (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[phosphonate] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 145265-37-8 CMF C38 H32 O8 P2

CM2

CRN 17026-42-5 CMF C18 H14 O8

Absolute stereochemistry. Rotation (+).

ΙT 133545-23-0P 133577-82-9P 133577-84-1P 133577-88-5P 133577-89-6P 145209-27-4P 145209-28-5P 145209-29-6P 145265-43-6P 145265-44-7P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (préparation and reduction of) RN133545-23-0 CAPLUS CN

Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)

PAGE 2-A

PAGE 3-A

RN 133577-82-9 CAPLUS

CN

Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-84-1 CAPLUS
CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-88-5 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)-, (R)- (9CI) (CA INDEX NAME)

RN 133577-89-6 CAPLUS
CN Phosphine oxide, [(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)

RN 145209-27-4 CAPLUS
CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

PAGE 1-A

PAGE 3-A

RN 145209-28-5 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis([1,1'-biphenyl]-4-yl)-, (R)- (9CI) (CA INDEX NAME)

145209-29-6 CAPLUS

RN

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis([1,1'-biphenyl]-4-yl)-, (S)- (9CI) (CA INDEX NAME)

RN 145265-43-6 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

RN 145265-44-7 CAPLUS

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-bis(4-methoxyphenyl)- (CA INDEX NAME)

RN 145209-12-7 CAPLUS

CN Phosphonic acid, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, tetraphenyl ester (9CI) (CA INDEX NAME)

RN 145209-14-9 CAPLUS
CN Phosphonic acid, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-,
P,P,P',P'-tetraethyl ester (CA INDEX NAME)

RN 145209-18-3 CAPLUS
CN Phosphonic dichloride, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis(CA INDEX NAME)

IT 145209-16-1P 145209-17-2P 145264-54-6P 145265-36-7P 145265-37-8P 145265-38-9P

145265-39-0P 145265-40-3P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of)

RN 145209-16-1 CAPLUS

CN Phosphonic acid, [6,6'-bis(methoxymethoxy)[1,1'-biphenyl]-2,2'-diyl]bis-, tetraphenyl ester, (R)- (9CI) (CA INDEX NAME)

RN 145209-17-2 CAPLUS

CN Phosphonic acid, [6,6'-bis(methoxymethoxy)[1,1'-biphenyl]-2,2'-diyl]bis-, tetraphenyl ester, (S)- (9CI) (CA INDEX NAME)

RN 145264-54-6 CAPLUS

CN Phosphonic acid, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis-, tetraethyl ester (9CI) (CA INDEX NAME)

RN 145265-36-7 CAPLUS

CN Phosphonic acid, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, tetraphenyl ester, (R)- (9CI) (CA INDEX NAME)

RN 145265-37-8 CAPLUS

CN Phosphonic acid, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, tetraphenyl ester, (S)- (9CI) (CA INDEX NAME)

RN 145265-38-9 CAPLUS

CN Phosphonic acid, P.P'-[(1S)-2',6-dimethoxy[1,1'-biphenyl]-2,6'-diyl]bis-, P,P,P',P'-tetraethyl ester (CA INDEX NAME)

RN 145265-39-0 CAPLUS

CN Phosphonic dichloride, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis-(9CI) (CA INDEX NAME)

RN 145265-40-3 CAPLUS

CN Phosphonic dichloride, P,P'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis- (CA INDEX NAME)

L3 ANSWER 29 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1993:59878 CAPLUS

DOCUMENT NUMBER: 118:59878

TITLE: Preparation of racemic and optically active

biphenyl-2,2-bisphosphines

INVENTOR(S): Broger, Emil Albin; Foricher, Joseph; Heiser, Bernd;

Schmid, Rudolf

PATENT ASSIGNEE(S): Hoffmann-La Roche, F., und Co. A.-G., Switz.

SOURCE: PCT Int. Appl., 34 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PA	PATENT NO.					KIND		DATE		API	PLICATION NO.			DATE
WO	9216 w·	536 JP,	us		A1		1992	1001		WO	1992-CH49			19920311
מיז		AT,		CH,	DE, A1						R, IT, LU, MC, 1992-905551			
	5303	36			B1		1996	0306						19920311
JP	R: 0550		BE,	CH,	DE, T	DK,					I, NL, SE 1992-504836			19920311
<del>-</del> .	3204 1350				В2 Т		2001 1996			AT	1992-905551			19920311
	5274	125			Ā		1993	1228		US	1992-949871 1991-805		Ą	19921113 19910315
PRIORII	I APP	٠ ١٧٠	INFO	• •	•					СН	1992-697 .	ž	A	19920305
OTHER S	OURCE	(S):			MARP	ΑТ	118:	59878	3	WO	1992-CH49	Ţ	Ν.	19920311

Ι

AB Title compds. (I; R = alkyl, alkoxy, protected OH; R1 = 5 ring atom containing heteroaryl; R2 = alkyl, alkoxy; n = 0-2), were prepared Thus, R-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(phosphonic acid di-Ph ester) (preparation given) in THF was added to the Grignard reagent from 2-iodofuran in THF and the mixture was stirred 1 h at 40° to give the bis(di-2-furylphosphine oxide), which was refluxed with Cl3SiH and Bu3N in xylene to give, after heating with aqueous NaOH, R-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(di-2-furylphosphine). I were used in asym. hydrogenation reactions.

IT 145265-36-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and Grignard reaction of, with iodofuran)

RN 145265-36-7 CAPLUS

CN Phosphonic acid, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-, tetraphenyl ester, (R)- (9CI) (CA INDEX NAME)

IT 145209-18-3P 145265-40-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and condensation of, with benzothiopehen derivative)

RN 145209-18-3 CAPLUS

CN Phosphonic dichloride, P,P'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis-(CA INDEX NAME)

RN 145265-40-3 CAPLUS

CN Phosphonic dichloride, P,P'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis- (CA INDEX NAME)

IT 145265-39-0P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and condensation of, with benzothiophene)

RN 145265-39-0 CAPLUS

CN Phosphonic dichloride, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis-(9CI) (CA INDEX NAME)

IT 145264-54-6P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation and conversion of, bis(phosphinyldichloride) derivative)

RN 145264-54-6 CAPLUS

CN Phosphonic acid, [(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis-, tetraethyl ester (9CI) (CA INDEX NAME)

IT 145306-47-4P 145306-48-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and decomposition of)

RN 145306-47-4 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [R-(R\*,R\*)]-, compd. with (R)-tetraphenyl (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[phosphonate] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 145265-36-7 CMF C38 H32 O8 P2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 145306-48-5 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [S-(R\*,R\*)]-, compd. with (S)-tetraphenyl (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[phosphonate] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 145265-37-8 CMF C38 H32 O8 P2

CM 2

CRN 17026-42-5

CMF C18 H14 O8

Absolute stereochemistry. Rotation (+).

RN 145214-58-0 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[di-2-furanyl-, (S)- (9CI) (CA INDEX NAME)

RN 145214-60-4 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[di-2-thienyl, (R)- (9CI) (CA INDEX NAME)

RN 145214-62-6 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[di-2-thienyl-, (S)- (9CI) (CA INDEX NAME)

RN 145214-64-8 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[di-3-furanyl-(9CI) (CA INDEX NAME)

RN 145214-70-6 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(benzo[b]thien-2-yl)-, (R)- (9CI) (CA INDEX NAME)

RN 145214-71-7 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(benzo[b]thien-2-yl)-, (S)- (9CI) (CA INDEX NAME)

RN145214-74-0 CAPLUS

Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(2-benzofuranyl)-, (R)- (9CI) (CA INDEX NAME) CN

RN 145214-75-1 CAPLUS CN

Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(2-benzofuranyl)-, (S)- (9CI) (CA INDEX NAME)

RN 145214-76-2 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(5-methyl-2-furanyl)- (9CI) (CA INDEX NAME)

RN 145214-77-3 CAPLUS

CN 1H-Pyrrole, 2,2',2'',2'''-[(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)diphosphinylidyne]tetrakis[1-methyl- (9CI) (CA INDEX NAME)

RN 145264-43-3 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[di-3-furanyl-, (R)- (9CI) (CA INDEX NAME)

RN 145264-44-4 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[di-3-furanyl-, (S)- (9CI) (CA INDEX NAME)

RN 145264-53-5 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(benzo[b]thien-2-yl)- (9CI) (CA INDEX NAME)

RN 145264-55-7 CAPLUS
CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(2-benzofuranyl)- (9CI) (CA INDEX NAME)

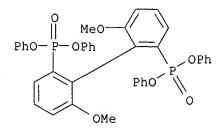
RN 145264-56-8 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(5-methyl-2-furanyl)-, (R)- (9CI) (CA INDEX NAME)

RN 145264-57-9 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(5-methyl-2-furanyl)-, (S)- (9CI) (CA INDEX NAME)

RN 145264-58-0 CAPLUS
CN 1H-Pyrrole, 2,2',2'',2'''-[(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)diphosphinylidyne]tetrakis[1-methyl-, (R)- (9CI) (CA INDEX NAME)



L3 ANSWER 30 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

1991:429462 CAPLUS

DOCUMENT NUMBER:

115:29462

TITLE:

Axially dissymmetric diphosphines in the biphenyl series: synthesis of (6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) ('MeO-BIPHEP') and analogs via an ortho-lithiation/iodination Ullmann-reaction

approach

AUTHOR(S):

Schmid, Rudolf; Foricher, Joseph; Cereghetti, Marco;

Schoenholzer, Peter

CORPORATE SOURCE:

Zent. Forschungseinheiten, F. Hoffmann-La Roche A.-G.,

Basel, CH-4002, Switz.

SOURCE:

Helvetica Chimica Acta (1991), 74(2), 370-89

CODEN: HCACAV; ISSN: 0018-019X

DOCUMENT TYPE:

Journal

LANGUAGE:

English

OTHER SOURCE(S):

CASREACT 115:29462

The new axially dissym. diphosphines (R)- and (S)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) [(R)- and (S)-I] and their analogs have been synthesized in enantiomerically pure form by a synthetic scheme which employs, as key steps, an ortho-lithiation/iodination reaction and a subsequent Ullmann reaction of the resulting iodides. The Ullmann reaction constitutes a new and efficient route to 2,2'-bis(phosphinoyl)-substituted biphenyl systems. Absolute configurations were established for (R)-I by x-ray anal. of the derived Pd complex. I proved to be as efficient as the previously described diphosphine (6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine) in enantioselective isomerizations and hydrogenations.

IT 133577-82-9P 133577-84-1P 133577-86-3P

133577-87-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of)

RN 133577-82-9 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN

CN Phosphine oxide, 1,1'-[(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-86-3 CAPLUS

CN Phosphine oxide, [(1S)-5,5',6,6'-tetramethoxy[1,1'-bipheny1]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133577-87-4 CAPLUS

CN Phosphine oxide, [(1R)-5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

IT 133545-15-0P 133545-18-3P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation and resolution of)

RN 133545-15-0 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1-diphenyl- (CA INDEX NAME)

RN 133545-18-3 CAPLUS
CN Phosphine oxide, (5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'diyl)bis[diphenyl- (9CI) (CA INDEX NAME)

CRN 133577-82-9 CMF C38 H32 O4 P2

1

CM

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 133577-85-2 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [S-(R\*,R\*)]-, compd. with (S)-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1.

CRN 133577-84-1 CMF C38 H32 O4 P2

CM 2

CRN 17026-42-5 CMF C18 H14 O8

Absolute stereochemistry. Rotation (+).

RN 133644-94-7 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [R-(R\*,R\*)]-, compd. with (S)-(5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-86-3 CMF C40 H36 O6 P2

CM 2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 134435-30-6 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-,  $[R-(R^*,R^*)]$ -, compd. with (5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133545-18-3 CMF C40 H36 O6 P2

CM 2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 134435-31-7 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [S-(R\*,R\*)]-, compd. with (R)-(5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-87-4 CMF C40 H36 O6 P2

CRN 17026-42-5 CMF C18 H14 O8

Absolute stereochemistry. Rotation (+).

L3 ANSWER 31 OF 31 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1991:247526 CAPLUS

DOCUMENT NUMBER:

114:247526

TITLE:

Preparation of chiral biphenyldiylbis(diphenylphosphin

e) derivatives and catalysts containing them

INVENTOR(S):

Cereghetti, Marco Dr; Foricher, Joseph; Heiser, Bernd

Dr; Schmid, Rudolf Dr

PATENT ASSIGNEE(S):

Hoffmann-La Roche, F., und Co. A.-G., Switz.

SOURCE:

Eur. Pat. Appl., 16 pp. CODEN: EPXXDW

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 398132 EP 398132	A2 A3	19901122 19910724	EP 1990-108686	19900509
EP 398132 R: AT, BE, CH,	B1 DE, DK	19950920 , FR, GB, IT	, LI, NL	
AT 128140 JP 03005492	T A	19951015 19910111	AT 1990-108686 JP 1990-128108	19900509 19900517
JP 2940626 US 5488172	B2 A	19990825 19960130	US 1994-294895	
PRIORITY APPLN. INFO.:	А	19960130	CH 1989-1905	19940823 A 19890518
			CH 1990-880 US 1990-521498	A 19900316 B1 19900510
			US 1992-884628 US 1993-152932	B1 19920515 B1 19931115
A				

OTHER SOURCE(S): MARPAT 114:247526

GI For diagram(s), see printed CA Issue.

AB The title compds. (I; R1 = alkyl; R2,R3 = H, alkoxy), were prepared for use as catalysts in enantioselective reactions (hydrogenations, rearrangements). Thus, (2-iodo-3-methoxyphenyl)diphenylphosphine oxide was dimerized using iodine-activated Cu in DMF to give 90.7% RS-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide). The latter was resolved using D- or L-dibenzoyltartaric acid and the R-enantiomer in Bu3N/xylene/HSiCl3 at 0° was treated with aqueous NaOH to give 97.3% R-II. Geraniol was hydrogenated to S-citronellol in 98.9% e.e. using Ru(R-II) (CF3CO2)2 catalyst and 60 bar H in MeOH at 20°.

IT 133577-83-0P 133577-85-2P 133644-94-7P

133644-95-8P 133644-96-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

CM 2

CRN 2743-38-6 CMF C18 H14 O8

Absolute stereochemistry. Rotation (-).

RN 133577-85-2 CAPLUS
CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [S-(R\*,R\*)]-, compd. with (S)-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-84-1 CMF C38 H32 O4 P2

CM 2

CRN 17026-42-5 CMF C18 H14 O8

Absolute stereochemistry. Rotation (+).

RN 133644-94-7 CAPLUS

CN Butanedioic acid, 2,3-bis(benzoyloxy)-, [R-(R\*,R\*)]-, compd. with (S)-(5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[diphenylphosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-86-3 CMF C40 H36 O6 P2

CM 2

CRN 2743-38-6

Absolute stereochemistry. Rotation (-).

RN · 133644-95-8 CAPLUS

CN Butanedioic acid, 2,3-bis[(4-methylbenzoyl)oxy]-, [R-(R\*,R\*)]-, compd. with (R)-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)phosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-88-5 CMF C42 H40 O4 P2

CM 2

CRN 32634-66-5 CMF C20 H18 O8

Absolute stereochemistry. Rotation (-).

RN 133644-96-9 CAPLUS

CN Butanedioic acid, 2,3-bis[(4-methylbenzoyl)oxy]-, [R-(R\*,R\*)]-, compd. with (S)-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)phosphine oxide] (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 133577-89-6 CMF C42 H40 O4 P2

CM 2

CRN 32634-66-5 CMF C20 H18 O8

Absolute stereochemistry. Rotation (-).

IT 133545-15-0P 133545-18-3P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation and reduction and resolution of)

RN 133545-15-0 CAPLUS

CN Phosphine oxide, 1,1'-(6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[1,1diphenyl- (CA INDEX NAME)

RN 133545-18-3 CAPLUS

CN Phosphine oxide, (5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'diyl)bis[diphenyl- (9CI) (CA INDEX NAME)

ΙT 133577-82-9P 133577-86-3P 133577-87-4P 133577-88-5P 133577-89-6P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of)

RN 133577-82-9 CAPLUS

CN Phosphine oxide, 1,1'-[(1R)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'diyl]bis[1,1-diphenyl- (CA INDEX NAME)

RN 133577-86-3 CAPLUS

CN Phosphine oxide, [(1S)-5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133577-87-4 CAPLUS

CN Phosphine oxide, [(1R)-5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl]bis[diphenyl- (9CI) (CA INDEX NAME)

RN 133577-88-5 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)-, (R)- (9CI) (CA INDEX NAME)

RN 133577-89-6 CAPLUS

CN Phosphine oxide, [(1S)-6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)

IT 133545-23-0P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation and resolution of)

RN 133545-23-0 CAPLUS

CN Phosphine oxide, (6,6'-dimethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME).

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IT 133545-31-0

RL: RCT (Reactant); RACT (Reactant or reagent)
 (reduction of)

RN 133545-31-0 CAPLUS

CN Phosphine oxide, (5,5',6,6'-tetramethoxy[1,1'-biphenyl]-2,2'-diyl)bis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)

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---Logging off of STN---

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Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	169.91	349.57
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
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